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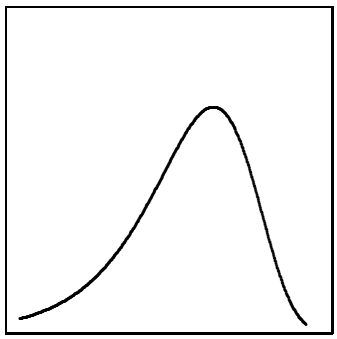
UNIVERSALITY IN KINETICS OF THE FIRST ORDER PHASE TRANSITIONS



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The general theory of the first order phase transition is presented.
Some universal dependences are established.

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To my parents

The results of the theoretical description of the second order phase transitions are so impressive especially in comparison with the development of the theory of the first order phase transitions. Really, despite the long way of the experimental investigation of the condensation from the end of the previous century there is no reliable description in frames of the modern principles of the theoretical physics. Traditionally the first order phase transition is regarded mainly as the condensation (or nucleation). After the creation of the classical theory of the condensation in 1930 - 1950 it seemed that the problem is reduced now to the investigation of the thermodynamic properties of the condensated substance. But the experimental investigations show that the central result of the classical theory of the condensation, i.e. the stationary rate of the condensation can not be reproduced experimentally. Really, there are many problems in the technical installation of the experiments but the discrepancy between the theory and experiment is so giant that it can not be explained only by the errors of experiment. The relative errors have the value of many orders of magnitudes and the current situation with the theoretical description can not be accepted as the satisfactory one.

So, the interest to present the theoretical description on the base of kinetics is rather natural.

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The analysis the classical theory of nucleation presented in [71], [72], [73], [74] and partially in [9] extracted the essential problems of the description of the rate of nucleation in the classical theory of nucleation. As far as the results of the mentioned papers are negative in the frames of the classical theory they were published only after the creation of the alternative approach presented here.

In [71] it is shown the possibility of the existence of the hidden thermodynamic parameters of the embryo description. These hidden parameters can not be observed in the properties of the super critical embryos and the bulk liquid. So, they can be extracted only from experiments on the nucleation itself. So, the nucleation rate can not be predicted here.

In [74] the hidden kinetic parameters were extracted. The possibility of the existence of the rapid variables of the embryo description was shown. These rapid variables can not be observed in the equilibrium

description and in the properties of the bulk liquid. But they are essential in the behavior of the critical embryo.

The problem of the stationary state of the critical embryo formation is one of the difficult questions in the classical theory and always was criticized. But before [72] only the non stationary evolution equation with the stationary kinetic coefficients was investigated. This can give only some weak (in few times) renormalizations of the nucleation rate and the leading exponential term remains the same. In the mentioned publication the pre critical region was analyzed and the possibility of the specific "activation barrier" was shown. This barrier leads to the giant renormalizations for the nucleation rate. Despite the qualitative character of the obtained results the functional dependencies coincides with the tendencies of experiments.

The investigation presented in [73] is rather more constructive. Today the reliable and reproducible experimental dependencies exist only for the substances from alcanes group. Here one can extract some characteristic interpolation formulas for the nucleation rate. In [73] the theoretical derivation of the mentioned dependence was given and the coefficients from the theory and experiment practically coincide. This allows to extract the connection of the microscopic correction with the structure of the substance.

In the process of the theoretical derivation the so-called "magic" numbers of the molecules were discovered. The deviation of the number of the molecules inside the embryo from the magic one leads to the deviation of the form of the embryo from the spherical one. This leads to the renormalization of the rate of nucleation.

The main conclusion from the first part of the presented investigation is the necessity of the new theory for the description of the phase transition.

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The main difference of the second order phase transition from the first order phase transition is the absence of the metastability. The first order phase transition occurs mainly due to creation and decay of the metastable state. So the phase transition has the kinetic character. The development in time determines the characteristics of the nucleation process. This feature was ignored by the classical theory of nucleation. The classical theory determines only the stationary (quasi stationary) characteristics. It is natural to construct the general theory for the whole evolution of the system during the phase transitions under the smooth

external conditions. We shall call such conditions with the smooth time behavior as the dynamic ones.

Meanwhile the classical theory of the nucleation gives the approximate write functional dependencies. It allows to use these dependencies in construction of the global theory of the phase transition. The first global theory for the homogeneous droplets formation was presented in [26] where only the first essential term in the expansion of the size spectrum of sizes was taken into account. The previous theories had postulated the model (and wrong) forms of the size spectrum without any justification. The theory for the further evolution of the phase transition was presented in [41] on the base of [26].

The creation of the approximate theory of the phase transition in [26] allowed to show in [7] the weak dependence of the characteristics of the phase transition on the microscopic corrections for the height of the activation barrier. The big errors in the stationary rate lead to the small errors in the characteristics of the phase transition. So, the possibility of the construction of the self consistent theory was obtained.

This consideration was made only for the collective consumption of the metastable phase. It means that every droplet consumes vapor from the volume where many other droplets exist. Only the homogeneous condensation was considered. But the process of condensation occurs mainly by the heterogeneous way. This leads to the principal difficulties. As far as it was shown in [82], [28], [27] the spectrum of sizes is the universal one in the special set of the variables. This universality from the first point of view resembles the universality in the second order phase transition. But here it has the specific kinetic nature. Now it can not be observed in some limited external conditions and depends of the regime of the droplets growth. In the heterogeneous case such a universality can be observed. As the result one needs the special approach presented in [40], [30]. Here the theory of the heterogeneous condensation in the dynamic conditions was constructed. The algebraic equation on the parameters of the condensation was solved in [43], [44].

The manner of investigation of the solution at the current level is different for the homogeneous and for the heterogeneous condensation. In the case of homogeneous condensation one can present the universal solution and in the case of heterogeneous condensation one has to use the method of the disbalanced iterations to get the approximate form of spectrum.

The connection between these approaches was established in [8] where the more precise way to determine the characteristics of the heteroge-

neous condensation was presented.

Again the weak dependence of the characteristics of the process on the microscopic corrections was shown. The theory became the self consistent and the stable for small perturbations. The problem of the applicability of the quasi stationary approximation was investigated in [77] where it was shown that

- one can use the quasi stationary approach

or

- the power of metastability is absolutely governed by the external conditions and the nonstationary effects are not important.

In the last case the total number of the droplets approximately coincides with that calculated in the stationary approximation. In the heterogeneous case the violation of the quasi stationary approach is possible only in the case when almost all heterogeneous centers are exhausted and the total number of the droplets coincides with the total number of the heterogeneous centers. So, here we see the simplification which allows to give the description in this case. The further development of the theory requires the consideration of the simultaneous action of the homogeneous and the heterogeneous ways of the droplets formation. It was done in [82].

After the creation of the theoretical description one can put the question of the justification of the experimental global laws of condensation. For the justification of the von Weimarn's law [29] the new power approximation was justified in [78]. On the base of this approximation this law unexplained for a rather long time was justified theoretically.

One can see that the theory of the condensation in the simplest variant is created now. It is present in the second chapter.

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All extracted dependencies can be spread over more complicated systems. At first the case of the multi component condensation was described. The complete theory of the evolution in the near critical region was given in [18]. The expression for the free energy with the surface excesses was constructed in [18] also. This solves the problem of the Wilemski-Renninger paradox and establishes the analytical topological structure of the free energy. The hierarchy of the kinetic coefficients was also considered. It leads to the cross of the activation barrier far from the saddle point. Also the hierarchy of the thermodynamic parameters

was extracted and on this base the iteration procedure was constructed. Also some specific approximations for the neighborhood of the saddle point were investigated.

The construction of the rate of nucleation allows to investigate the global evolution. In [79] the multidimensional kinetic equation was investigated and the method of the Green function was presented. The reduction of the current situation to the one dimensional case was also observed. In [79] the decay of the binary mixture was investigated. In [80] the binary condensation was investigated in the dynamic conditions. The analogous problems in the multi component case was solved in [75], [9]. In all situations the kinetic problem can be reduced to the one dimensional case.

All these problems were solved in the third chapter.

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The further development of the theory contains the consideration of the few types of the heterogeneous centers. In this situation the difference between the decay and the dynamic conditions is fundamental. Under the dynamic conditions the exhaustion of the heterogeneous centers of the different types occurs in the different moments of time. In the situation of decay the condensation of the different types occur in one and the same time. The already known methods can not lead to the result here. One can extract and investigate four characteristic situations: the decay on the few types of the heterogeneous centers [67], the decay on the continuous activity spectrum of heterogeneous centers [68], the condensation on the few types of the heterogeneous centers under the dynamic conditions [69], the condensation on the continuous activity spectrum under the dynamic conditions [66].

Here the solution can be given by the different manners. In every case one has to justify the specific ansatz for the size spectrum. The most difficult case is the third one. Here one must describe the condensation under the nonlinear behavior of the external conditions. It was done in [70].

One has to stress that the universality of the spectrums allows to formulate the required ansatz and to reduce the problems to the algebraic ones. Here the universality is already the instrument of investigation. During the process of the investigation of these problems some other important universal dependencies were established. Also the inclusion of the heterogeneous condensation on one type of heterogeneous centers into the more general situation with the universal behavior is presented.

The connection between the relative activity and the number of the centers can be shown.

Beside the concrete construction of the solution the new universal features of the process were extracted. Also the natural initial conditions were formulated.

All these problems form the forth chapter.

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We have to stress that until the current moment all theoretical constructions were made only for the collective regime of the vapor consumption. Meanwhile it is evident that every droplet initiates the profile of the vapor density. The new droplets appear on the superposition of these profiles. The construction of the theory in this situation is very complicate. But with the help of the conception of the universal form of the size spectrum it can be done.

During the consideration of the profile one can see the sharp Hevisaid-type character of the behavior of the rate of nucleation in some spatial point far from the already existed droplet. So the superposition of the profiles can be split. One can consider the separate droplet and consider the evolution in terms of the exhausted volumes. But even after such simplification one can not formulate the mathematical model and the system of the condensation equations.

The possibility to solve this problem is connected with the sharp character of the substance consumption by the separate droplet. The same property is also responsible for the rapid convergence of the iteration procedure in the method of the disbalanced iterations. Here it is connected with the proximity of the results of the different models which estimates the results of the process from below and from above.

The solution of the problem of the theoretical description under the profiles of the density is given in [81]. The generalization of the theory for the temperature profiles and for the heterogeneous condensation is given in [81], [83].

The leading feature of the obtained solution is the coincidence of the functional forms of the spectrums in the situation of the pure free molecular regime of the vapor consumption and in the situation of the profile of the density. This allows to describe the continuous transition from one limit regime to another limit one by the solution of the algebraic problem.

The theory of the condensation with the profiles of the density forms the fifth chapter.

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One of the model for the solution of the situation with the density profiles has the solution which coincides after the certain renormalizations with the first iteration in the method of the disbalanced iterations. This expression can be reduced to the absolutely universal form which doesn't depend on the regime of the vapor consumption. The law is approximate, but this universality is very important in the context of the weak dependence on the microscopic corrections. Now we have this connection [81].

The universality is transformed from the property as the instrument of investigation to the process to the fundamental feature which allows to formulate the system of equations of the condensation [83].

The next step is to show such universality in the case of the temperature profiles. It can be made by the certain renormalizations [83].

The approximate universality of the spectrum can be established also in the condensation on the continuous activity spectrum of the heterogeneous centers [84].

The investigation of the condensation in the system with the source of the heterogeneous centers can be also fulfilled with the help of the conception of the universality of spectrum of the droplets sizes [76].

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In the investigation of the spatially unhomogeneous systems the same universal form of the spectrum on the spatial variable can be justified [84]. Here the form of the spectrum is established. Earlier only the model forms for the spectrum were suggested in this situation.

Also the analogy between the universality of the Lifshiz-Slesov theory of coalescence and the theory constructed here was observed.

The development of the conception of the universality of the size spectrum is presented in the sixth chapter.

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The result of the investigation is the creation of the theory of the first order phase transition. The conception of the universality allows to solve all considered problems and can be regarded as the general feature of the first order phase transition.

Chapter 1

Current state of the nucleation theory

1.1 The main conceptions of the classical nucleation theory

1.1.1 Stationary intensity of the droplets formation

The central problem of the classical nucleation theory is the the derivation of the stationary rate of nucleation. It was done in 1940-ies in [6], [1], [31], [3], [50], [2]. In these papers the quantity of the super critical embryos appeared in the unit of time was found. In other terms one can say that the stationary flow I_s in the space of sizes was calculated[1].

Later this expression was corrected in [4], [25] and in the other papers. In the expression for the stationary rate of nucleation there is the value of the height of activation barrier of nucleation ΔF.

Two important characteristics of the supersaturation were measured at that time in the experiments: the "rain" limit - in the cubic centimeter of the chamber the few drops were formed; the "smog" limit - in the cubic centimeter of the chamber many small droplets were formed. These values were introduced by Wilson who constructed the chamber and began these investigations [52].

[1] In the stationary rate of the heterogeneous condensation I_s one has to fix the quantity of the free (unoccupied by the super critical droplets) heterogeneous centers.

Intensity of the droplets formation in the classical theory of nucleation.

Here we shall get the expression for the stationary rate of nucleation in frames of the classical theory in the heterogeneous case. The power of metastability can be characterized by the value of the supersaturation

$$\zeta = n/n_\infty - 1 \quad , \tag{1.1.1}$$

where n is the molecules number density in the vapor, n_∞ is the molecules number density in the vapor saturated over the plane surface of the bulk liquid.

The presence of the heterogeneous centers leads to the decreasing of the value of the activation barrier of nucleation. If the supersaturation in lower than the value which corresponds to the disappearing of the activation barrier then the free energy of the embryo formation F_ν (as the function of the number ν inside the embryo) has at least one maximum which corresponds to the critical embryo and one minimum which corresponds to the equilibrium embryo. The critical embryo is greater than the equilibrium one and in the process of the fluctuation growth the equilibrium embryo has to overcome the activation barrier.

Denote the points of the maximum and the minimum of F_ν as ν_c and ν_e correspondingly. Then ν_e is the number of the molecules inside the equilibrium embryo and ν_c is the number of the molecules inside the critical embryo. Indexes c, e denote the values for these embryos. The free energy of the embryo formation F_ν can be determined only near the extremal points as far as it can be determined only for the object in the state of equilibrium. May be there are many minimums and maximums, then one has to choose the maximum which corresponds to embryo greater than the equilibrium one and the minimum which corresponds to the embryo less than the critical one. We shall measure the free energy (as all energy like magnitudes) in the units of $k_B T$, where k_B is the Bolzman constant and T is the temperature.

Ordinary one can find F_ν only for the values of ν_e and ν_c which are many times greater than unity. One can apply thermodynamics only then there are many molecules of the substance inside the embryo. So, the conditions

$$\nu_c \gg 1 \quad , \quad \nu_e \gg 1 \tag{1.1.2}$$

are the natural requirements from the thermodynamic description. Only in this case one can speak about the macroscopic description of the embryo.

When the supersaturation grows then the height of the activation barrier decreases. Extract the "threshold" region of the supersaturation which is characterized by the inequality

$$\exp(\Delta F) \gg 1 \quad , \quad \Delta F = F_{\nu_c} - F_{\nu_e} \quad . \tag{1.1.3}$$

If the activation barrier is absent then all heterogeneous centers become the centers of the droplets which grow regularly. This solves the problem of the evolution. In the case of the small activation barrier the steepens descent method from the classical theory of nucleation can not be applied.

Introduce the width $\Delta\nu_e$ of the equilibrium region and the halfwidht $\Delta\nu_c$ of the critical region as the values from the following equations

$$\Delta\nu_e = \sum_{\nu \le (\nu_c+\nu_e)/2} \exp(-F_\nu + F_{\nu_c}) \ , \tag{1.1.4}$$

$$\Delta\nu_c = \sum_{\nu \ge (\nu_c+\nu_e)/2} \exp(-F_{\nu_c} + F_\nu)\ \pi^{-1/2} \quad . \tag{1.1.5}$$

In the case of the high activation barrier the terms of the series in the previous equations are already negligible near the boundary of the region of summation. The region $\nu \le \nu_c - \Delta\nu_c$ is called as the precritical region, the region $|\nu - \nu_c| \le \Delta\nu_c$ is called as the critical region, the region $\nu \ge \nu_c + \Delta\nu_c$ is called as the post critical region and the region $\nu \ge (2 \div 3)^3 \nu_c$ is the super critical region.

The super critical region is extracted by the fact that the embryos with $\nu \ge (2 \div 3)^3 \nu_c$ grows regularly and the flow of the ejected molecules can be well approximated by the flow of the molecules adsorbed by the plane surface. For the free molecular regime of the substance exchange the law of growth can be written in the following form:

$$\frac{d\rho}{dt} = \frac{\alpha\zeta}{\tau} \quad , \tag{1.1.6}$$

where

$$\rho \equiv \nu^{1/3} \tag{1.1.7}$$

is the linear size of the molecule,

$$\tau = 12[(36\pi v_l^2)^{1/3} n_\infty v_T]^{-1} \tag{1.1.8}$$

is the value with the order of the characteristic time between the sequential collisions of the given molecule with the other molecules in the

vapor, v_l is the volume for one molecule in the liquid phase (ordinary one can neglect the compression of the liquid), v_T - is the mean velocity of the molecules of the condensated substance, α is the condensation coefficient. We shall use the term "droplets" for the super critical embryos. One can describe droplets by the variable ρ. It is convenient to use this variable because the rate of growth doesn't depend on the concrete value of this characteristic.

In the threshold region of the supersaturations the following inequalities

$$\frac{\Delta\nu_c}{\nu_c} \ll 1 \quad , \Delta\nu_c \gg 1 \tag{1.1.9}$$

are valid for the majority of the types of the heterogeneous centers. For $\Delta\nu_c$ with the help of the square approximation of the free energy in the critical region one can obtain

$$\Delta\nu_c = |\frac{2}{\frac{\partial^2 F_\nu}{\partial\nu^2}|_{\nu=\nu_c}}|^{1/2} \quad . \tag{1.1.10}$$

Really, the precise expression can be written only for the known behavior of F_ν. The qualitative picture of the applicability of the last expression is based on the fact that the influence of the heterogeneous center on the molecules near the surface of the critical embryo is weak as far as $\nu_c \gg 1$. So, the action of the nuclei on the behavior of F_ν near ν_c is rather weak and one can approximately assume that in the critical region the difference of the free energy of the heterogeneous embryo formation differs from the homogeneous formation free energy by the constant value. This leads to the applicability of this expression as far as it is valid for the homogeneous case. In the condensation on the ions (the long range potential) the influence of the heterogeneous center is essential for F_ν in the critical region. But even in this situation this expression is rather precise which can be justified by some concrete calculations. This consideration is also the base for the application of the steepens descent method in the further constructions.

This feature also leads to the solution of the problem to determine the height of the activation barrier. The number of the critical embryo can be found from the homogeneous expression and later it can be made more precise by corrections[2]. Then it is sufficient to calculate the free energy according to the explicit formula.

[2]It is necessary to take into account the difference of the structure of the center of the embryo from the homogeneous case. Approximately it doesn't depend on the supersaturation.

The situation with the equilibrium region is different. The formation of the equilibrium embryo occurs due to the action of the heterogeneous center. So, the inequalities analogous to (1.1.9) can be violated. The square approximation isn't valid, to get $\Delta\nu_e$ it is necessary to calculate the seria in the definition of this value.

The simplification in this case comes from the weak dependence of all characteristics of the equilibrium embryo from the supersaturation. The width of the equilibrium region depends weakly from the supersaturation. The energy of the solvatation depends on the supersaturation weakly[3]. In further formulas one can approximate these values by the constants.

The inequalities (1.1.9) allow to substitute in the critical region and in the post critical region the Bekker-Zeldovitch equation [3] in the form of the finite differences for the number n_ν of the embryos of ν molecules by the differential form. In the continuous form it can be written as

$$\frac{\partial n_\nu}{\partial t} = -\frac{\partial}{\partial \nu}\{(W_\nu^+ - W_\nu^-)n_\nu - \frac{1}{2}(W_\nu^+ + W_\nu^-)\frac{\partial n_\nu}{\partial \nu}\} \qquad (1.1.11)$$

where W_ν^+ and W_ν^- are the numbers of the absorbed and ejected molecules in the unit of time. The last equation is the continuity equation for the function n_ν with the flow J_ν along ν

$$J_\nu = \{(W_\nu^+ - W_\nu^-)n_\nu - \frac{1}{2}(W_\nu^+ + W_\nu^-)\frac{\partial n_\nu}{\partial \nu}\} \quad . \qquad (1.1.12)$$

In the critical region and in the case $\zeta \ll 1$ also in the post critical region the obtained equation transforms into

$$\frac{\partial n_\nu}{\partial t} = -\frac{\partial J_\nu}{\partial \nu} \quad , \qquad (1.1.13)$$

$$J_\nu = -W_\nu^+ n_\nu \frac{\partial F_\nu}{\partial \nu} - W_\nu^+ \frac{\partial n_\nu}{\partial \nu} \quad .$$

If the supersaturation and the density of the free heterogeneous centers η are constants, then in the critical region and in the post critical region there is the stationary distribution n_ν^s. After the integration of the kinetic equation in the critical region one can find

$$n_\nu^s = I_s \exp(-F_\nu) \int_\nu^\infty \frac{d\nu'}{W_{\nu'}^+} \exp(F_{\nu'}) \quad , \qquad (1.1.14)$$

[3]The inequality $\nu_e \gg 1$ isn't so essential.

where I_s is the stationary flow which doesn't depend on ν. To determine I_s one has to suppose that there is the equilibrium distribution

$$n_\nu^e = \frac{\eta}{\Delta\nu_e}\exp(-F_\nu + F_{\nu_e}) \tag{1.1.15}$$

in the precritical region.

The validity of this supposition is guaranteed by the absence of the other maximums of the free energy with the height of the order F_{ν_c}. When $\nu \leq \nu_c - \Delta\nu_c$ the distribution n_ν^s has to be transformed to n_ν^e. One has use the steepens descent method after the substitution of the lower limit of integration to $-\infty$ due to (1.1.9). On the lower boundary of the critical region the distribution n_ν^s must transform to n_ν^e. So, one can come to

$$I_s = \frac{W_{\nu_c}^+ \eta \exp(-\Delta F)}{\pi^{1/2}\Delta\nu_e\Delta\nu_c} \quad . \tag{1.1.16}$$

The value of $W_{\nu_c}^+$ can be found from the fact that the critical embryo is in the equilibrium with the vapor. So, after the gas dynamic calculations one can come to the following expression for I_s:

$$I_s = \frac{3\nu_c^{2/3}\alpha(1+\zeta)\eta\exp(-\Delta F)}{\pi^{1/2}\tau\Delta\nu_e\Delta\nu_c} \quad . \tag{1.1.17}$$

In the case of the homogeneous condensation the flow $\bar{I}_s$ can be found analogously

$$\bar{I}_s = \sqrt{\frac{a}{\pi}}\alpha(1+\zeta)^2 n_\infty \exp(-\bar{F}_{\nu_c})/\tau \tag{1.1.18}$$

where

$$a = (\frac{4\pi\gamma}{k_b T})(\frac{3v_l}{4\pi})^{2/3} \quad ,$$

γ is the surface tension and the values for the homogeneous case are denoted by "bar". As far as $\bar{F}_{\nu_c}$ has the explicit formula the value of $\Delta\bar{\nu}_c$ can be calculated explicitly. The value of $\Delta\bar{\nu}_e$ is equal to unity[4].

Later we shall use for the time $\bar{t}_s$ of the establishing of the stationary distribution in the critical region the estimate of Zeldowitch

$$\bar{t}_s = \frac{(\Delta\bar{\nu}_c)^2}{W_{\nu_c}^+}$$

[4]The additional normalizing factor will be discussed later.

and the estimate of Kuni-Grinin [51]

$$\bar{t}_s = \frac{\rho_s^3 \tau}{\zeta + 1} \sqrt{8a} \tag{1.1.19}$$

where $\rho_s = (2 \div 3)\rho_c$. The last estimate is the estimate from above for $\bar{t}_s$. It is greater than the estimate of Zeldowitch because it guarantees the stationary distribution in the region $\nu \leq (2 \div 3)^3 \nu_c$.

In the case of the heterogeneous condensation one can have as the estimate of Zeldowitch

$$t_s = \frac{(\Delta\nu_c)^2}{W_{\nu_c}^+} \tag{1.1.20}$$

The special features of the determination of the height of the activation barrier of nucleation

After the construction of the theoretical expression for the stationary rate of nucleation it was checked in many experiments. The difference between the theoretical value of the nucleation rate and the experimental value was giant ($10^4 - 10^{17}$ times).

* * *

According to the expression for I_s or for $\bar{I}_s$ these values have the sharp dependence on the height of the activation barrier ΔF or $\bar{F}_{\nu_c}$. In the case of the homogeneous condensation $\bar{F}_{\nu_c}$ has the value greater than 40-50. This value is the argument of exponent (the small absolute value of exponent is compensated by the big values of the order of the Avogadro number). So, the small relative error in $\bar{F}_{\nu_c}$ leads to the great error in $\bar{I}_s$. This forms the main problem of the classical theory of nucleation.

So, the main efforts were intended to get the most precise values for the free energy of the embryo formation.

In 1952 Reiss [54] got the expression for the free energy of the critical embryo with the help of the methods of the statistical mechanics. The way of calculation is rather simple - to calculate the configurational integral. But the problem is how to fulfill the integration over the thousands of variables. In the calculation of the configurational integral Reiss had to use the same suppositions as in the thermodynamics - the homogeneous character of the embryo and of the vapor, the spherical form of the embryo, etc. Now these suppositions are used in the definition of the subintegral functions in the specific regions of integration. So, the expression is rather analogous to the thermodynamic one.

In 1962 Lothe and Pound [4] gave the derivation of the expression for the free energy with the help of the quantum mechanics. The rotational

corrections for the free energy lead to the corrections in the stationary rate in 10^{17} times. But this correction doesn't lead to the coincidence between the theoretical and the experimental results.

Reiss and Katz [25] corrected the expression of Lothe and Pound. But the difference between these approaches is the style of the fixation of the center of the embryo in space. The long discussion in 1960-ies, 1970-ies didn't lead to the resolution of these contradictions.

Density functional theories

The application of the theory of the simple liquids seems to be fruitful for the theory of nucleation. This opportunity was used by [17], [21] for the different potentials of the interaction between molecules. This approach is called the density functional approach.

The main feature of such approach is rather evident and attractive - to determine all necessary features of the critical fluctuation (one can regard the critical embryo as the critical fluctuation) with the help of the theory of the simple liquids. This base leads to the density functional Ω.

From the first point of view the method of the density functional can be regarded as the alternative to the classical theory of nucleation. Really, the main factor in the expression for the stationary flow is the exponent based on the free energy of the critical fluctuation. Both the classical theory of nucleation and the density functional theory use this fact.

Really, the more accurate calculation of the free energy has some advantages. But even this approach has some problems. The main problem is the account of the pair correlations inside the critical fluctuation. It is essential to know whether this problem leads to the big correction in the rate of nucleation.

This problem has at least the following aspects:

- The precise expression for the correlation function is the unknown one.
- The existence of the profile of the density means that the situation is unhomogeneous. In the unhomogeneous situation it is difficult to get even some estimates for the correlation function.
- Even in the homogeneous regions the values of the temperature and the pressure don't satisfy the conditions of the phase coexistence. So, one can speak only about the analytical expansion of the expressions for the correlation functions.

Beside the fundamental theoretical problems there are many problems in the technical installation of this method. The main among them are

- The split of the potential into the short range part and the long range part.
- The substitution of the short range potential by the hard core potential.
- The approximate character of the Carnakhan-Starling expression for the chemical potential of the hard core potential.
- The linear approximation for the long range part influence of the chemical potential.

We shall analyze the main problem connected with the pair correlations. The concrete calculations show the sharp dependence of the difference between the rates of nucleation in the classical theory of nucleation and the density functional theory[5]. Even with the variations in the surface tension initiated by correlations one can not attain the coincidence of the results or extract any tendency in their deviations.

The same can be made from the qualitative estimates. The unknown form of the correlation function in the unhomogeneous region leads to the unknown value of the distance l between the surface of tension and the equimolecular surface. The difference has the scale of the distance between molecules in the liquid. This difference leads to the essential differences in the rate of nucleation.

In the situation with the unoccupied surface layer the expression for the free energy has the form $F = a(\rho + l)^2 - b\rho^3$. Then $\rho_c \approx \rho_c(l = 0) + l$, $|F_c(l) - F_c(l = 0)|/F_c(l = 0) \approx 6l/\rho_c(l = 0)$. The variations are very essential in this case. For the supercoccupied surface layer one can get $F = a\rho^2 - b(\rho + l)^3$. In the leading term in ρ one can get the renormalization of the surface tension $a \to a - 3bl$. As far as F_c is proportional to the cube of the surface tension one can get the variations in the value which are big in the relative units. The variations in the rate of nucleation are giant.

* * *

[5]Correlations have to be taken into account also in the plain problem of the calculation of the surface tension.

Now the role of correlations is evident. This role is fatal for the density functional theory. The knowledge of the rate of the nucleation is equivalent to the knowledge of the pair correlation function (or some functional of the pair correlation function). The inverse problem can give the information about the characteristics of the pair correlation function. The experimental conditions are rather attractive to obtain the correlations. But for the theory of nucleation this conclusion means the absence of method of construction of the concrete value of the rate of nucleation.

This consideration allows now to reject all wonderful recipes which give the precise coincidence between the theory and the experiment. We see now that the problem lies in the form of the correlation function in the unhomogeneous surface region. This problem can not be solved in the current state of the molecular and statistical physics.

* * *

In the last years there appeared some publications which give the empirical expressions for the free energy with the precise computer calculations [35]. Even with the help of the computer calculation of the configurational integral for the embryo there remain many problems connected with the place of the embryo formation, with the correct determination of the ensemble and so on.

Also one can stress the approaches which establish the functional form for the free energy and choose some constants to fit the experimental data [55].

Specific features of the derivation of the expression for the stationary rate of nucleation

The derivation of the expression for $\bar{I}_s$ and I_s needs some commentaries:

- The value of the free energy can be determined only for the critical and for the equilibrium embryos as the equilibrium objects.

  The value F_ν can be gotten formally as the value from the set of equations

  $$\frac{W_\nu^+}{W_{\nu+1}^-} = \exp(F_\nu - F_{\nu+1}) \quad . \tag{1.1.21}$$

  The analytical expansion corresponds to the supposition that W_ν^- doesn't depend on the state of the vapor. This supposition is the approximation.

The approximate value F_ν for the arbitrary ν leads to some errors in $\Delta\nu_c$ and in $\Delta\nu_e$. It is natural to suppose that the mentioned approximation is rather precise and these errors are rather small.

- The rate of nucleation can be reduced by the specific behavior of the free energy for the small embryos.

  Due to the negative value of the second derivative for the analytical expansion of the expression for the free energy as the function of ν the process of coagulation is energetically unprofitable[6]. For the heterogeneous condensation the process of coagulation can be important.

- The presence of the heterogeneous centers reduces the value of the supersaturation to the value

$$\zeta - \tilde{\zeta} = \frac{\nu_e \eta}{n_\infty} \quad . \tag{1.1.22}$$

  To exclude the influence of the small embryos (and in the case of the heterogeneous condensation the influence of the equilibrium embryos) on the rate of nucleation it is necessary

$$\frac{I_s(\zeta) - I_s(\tilde{\zeta})}{I_s(\zeta)} \ll 1 \quad . \tag{1.1.23}$$

  In the opposite situation this influence has to be taken into account.

* * *

We see that the relatively small errors in the free energy of the critical embryo leads to the giant errors in the rate of nucleation.

One can suppose that the microscopic correction can be described by the seria in the inverse powers of ρ and by the term proportional to $\ln \rho$. Even when the relative influence of these terms in ΔF is small the value of $\exp(-\Delta F)$ is renormalized in thousands times.

The relative influence of the microscopic corrections in $d\Delta F(\zeta)/d\zeta$ will be small. Then the further theory will state that the microscopic corrections don't act essentially on the main characteristic of the global evolution during the condensation.

[6] In the region of the small sizes the capillary approximation can be violated and it can lead to the coagulation.

1.1.2 Kinetic problems of the condensation

The first investigations in the kinetics of the condensation are made by Zeldovitch [3] who gave the estimate for the time of relaxation and by Tunickii [50] who considered the decay of the metastable state.

The evolution of the system after the instantaneous creation of the initial supersaturation, i.e. the situation of the metastable state decay, was investigated to check the conditions for the measurements of the stationary rate of nucleation. Here only the end of the process of the unperturbed formation of the droplets was interesting. This leads to the consideration of the cut off of the droplets formation due to the requirements of the problem but not due to the physical reasons. Ordinary it was made without appropriate justifications. In the cited paper by Tunickii and some other ones the approximation for the spectrum of sizes was suggested as the rectangular one due to the cut off. This was done without any justification only on the base of the experimental results and tendencies. Only in [59] some justifications were presented.

It is necessary to stress the approach [48] which is based on the linearization of the kinetic equation. This linearization without any estimates can not be accepted as the rigorous theory.

In [60] the consideration was based on some model forms of the spectrum also without any justifications.

In [61] the formal iteration method of solution of the kinetic equation was presented. It allows to find the solution with a rather high precision, but only in the homogeneous case. The formal generalization for the arbitrary Knudsen numbers was presented in [47]. In [49] the theory of the heterogeneous condensation after the instantaneous creation of the supersaturation was constructed. As far as the concept of the disbalanced iterations was unknown only the limit cases were considered. In these situations all heterogeneous centers are exhausted or practically remain unexhausted.

We have to note that the conditions of decay are rather specific and it is difficult to ensure such conditions in the experiment. The supersaturation has to grow at first very rapidly and then has to remain constant during the rather long period. These conditions require the special installation of the experiment.

* * *

The more natural conditions are the conditions of the continuous smooth growth of the imaginary ideal supersaturation, i.e. the supersaturation governed only by the external conditions. At first the theory

of condensation was considered in [39]. In this paper the problem of the theoretical description of the condensation in the adiabatic flow was considered. The connection between the quasi stationary approximation and the macroscopic description of the critical embryo has not been established. That why a special regime of the "slow cooling" was extracted. The integral term of the balance equation was calculated on the base of the steepens descent method. But for the different derivatives in equations for the different parameters of the spectrum the different models for the size spectrum were used. This was done without any justification which destroys the self consistency of the theory.

The relative deviation of the temperature was chosen for the variable describing the evolution. The more general characteristic for the rate of nucleation is the supersaturation. Namely this characteristic is to be linearized which has been done in [26]. The procedure now is the self consistent one. In [41] also the evolution of the system until the coalescence [45] has been presented.

The processes of the heterogeneous condensation were considered in many papers, but rather formally - without any account of the exhaustion of the free heterogeneous centers. The simultaneous formal account of homogeneous and heterogeneous condensation in the cited paper by Raiser isn't valid as it will be seen later.

Also one has to mention [63] as the example of the application of the model forms for the spectrum of sizes. The triangle approximation used in the cited paper isn't valid at all. The "rapid" regime of condensation considered in the cited paper can not be realized under the thermodynamic description of the critical embryo.

In [42] in the consideration of the homogeneous condensation process the iteration procedure was applied. But in the cited paper every iteration requires the special choice of parameters. As the result one can not use the estimating properties of the operators and get the strict estimates for the precision of the iterations.

The unique choice of the parameters in the iterations and the guarantered estimates for the precision of the iteration was presented in [40] where the process of the heterogeneous condensation was also considered.

In the consideration of the homogeneous condensation the application of the iteration method is rather standard. In the process of the heterogeneous condensation one has to apply the new method - the method of the disbalanced iterations. One has to split the expression for the quantity of the substance into two parts by the appropriate choice which allows to construct the disbalanced iterations. This split has to use the

special properties of the operators in the split parts. The disballancing of the iterations is compensated by the opportunity of the analytical calculations.

* * *

After the brief review of the current state of the theory of nucleation it is possible to investigate the problems of the classical theory of nucleation. One has to analyze the suppositions of the classical theory and estimate the opportunities to overcome these problems.

1.2 Hidden thermodynamic parameters.

One shall start the analysis of the problems in the classical theory of nucleation from the existence of the hidden thermodynamic parameters of the embryo description. Let us call the hidden parameter of the embryo as the order parameter.

The order parameter must be hidden - it must have the normal value in the bulk phase.

The formal analogy of the situation under the consideration and the theory of the binary condensation [5] will help to give the theoretical derivation. In the capillarity approximation one can get for the free energy of the embryo: $F = a\nu^{2/3} - b\nu$, where the parameters a and b are some functions of the intensive parameters. The physical sense of a is the dimensionless surface tension and b is the excess of the chemical potential.

Denote the order parameter via n. The partial volume v_l for the molecule in the liquid phase is the certain function of n. So, parameters a, b as the functions of v_l are the functions of n.

The most simple method of consideration will appear if we denote the variable of description as the surface energy in power $3/2$. Denote it via ν. Then we get $F = \nu^{2/3} - B\nu$ with some renormalized value of the excess of the chemical potential B.

There are at least two problems connected with the order parameter - the surface excess problem and the bulk capillarity problem. At first one has to mention the surface excess problem. Really, the situation under the consideration resembles the binary condensation. So, the Wilemski-Renninger paradox has to be taken into account. It means that the channel of nucleation doesn't coincide with the minimum (may be the local one) of the function B. The formal derivation is absolutely equivalent to the binary nucleation and it will be completely discussed in

the third chapter. In any case this will lead to the essential reconsideration of the free energy at the saddle point (as it will be seen in the third chapter the position must be reconsidered) and to the reconsideration of the rate of nucleation.

The deviations in the free energy in the bulk capillarity problem may be even more essential than in the surface problem. Consider the standard form for the free energy

$$F = a(n)\nu^{2/3} - B(n)\nu.$$

Suppose that there are at least two minimums of B (two channels of nucleation)[7] and

$$n_1 < n_2,$$

where the lower index denotes the number of the channel. The first channel corresponds to the ordered embryo and the second channel corresponds to the disordered embryo.

Suppose that

$$B(n_1) > B(n_2).$$

Then the first channel is the asymptotically leading one. Really, asymptotically

$$F = -B(n)\nu.$$

If

$$a(n_1)(\frac{2a(n_1)}{3B(n_1)})^2 > a(n_2)(\frac{2a(n_2)}{3B(n_2)})^2,$$

then energetically the leading is the second channel.

One has to use the Gibbs adsorption equation and to take into account the Wilemski-Renninger paradox. But the qualitative conclusions will be the same.

The condensation occurs through the second channel. But the properties of the bulk liquid are observed in the first channel. May be one can know the intensive parameters only in the state of equilibrium in the first channel.

Now the theory of nucleation becomes the separate theory which has no evident connection with the thermodynamic bulk parameters of the condensated substance.

Note that coagulation leads to the transmision from the second channel to the first one, which is asymptotically leading.

[7]Here we use the topological properties in the binary condensation, see the third chapter.

Note also that the disordered value of parameter is specific also for the condensation of the macroscopic surfaces. Really, it is rather difficult to choose the macroscopic surface of another material in such a way that it corresponds to the order distance in the condensated liquid. So, the surface initiates the disordered value of parameter.

* * *

The same effects can be observed also without the mentioned conditions. Note that the mentioned parameters are the local characteristics, but depend on the neighborhood of the observation point. The characteristic size is the length of correlations. Ordinary, far from the critical (the second order phase transition) point this distance has the order of the distance between the molecules. But the size of correlations may be in some cases greater than the size of the critical embryo. In such a case one can speak about the collective behavior of the molecules inside the embryo.

So,

$$n(r) = \int dr' \hat{n}(r') K(|r - r'|),$$

where K is the kernel of averaging, $\hat{n}$ is the microscopic functional analog of n. Function K is localized in the region $|r - r'| < r_{corr}$ where r_{corr} is the radius of the correlations.

Suppose that the ordered state is energetically and asymptotically profitable. After the beginning of the condensation it is necessary to create the region with the size r_{corr}. The free energy to create such an object may be greater than the ordinary value in the capillarity approximation. This will lead to an error.

* * *

Another possibility of deviation is connected with the difference between the condensation on the disordered surface and the condensation in the ordered channel. If v_l has the maximum in transition from the ordered parameter to disordered one then there appears the barrier of the condensation. It may have the value greater than the old barrier of condensation[8]. The asymptotically leading channel can not be attained due to the big value of the barrier between the channels. This was the third energetic possibility of deviation in the rate of nucleation.

[8]Now there is no great number of the candidates for the center of embryo as the number of molecules in the vapor.

* * *

Beside the energetic difficulty there may occur the kinetic difficulty. The embryo is always embedded in the vapor and can not go away from the boundary with the vapor. In the fluctuations in the bulk liquid the situation is quite opposite. Suppose that the orientation of the molecule can be changed only in the vapor[9]. So, until the size r_{corr} the fluctuation has to be near the surface. But it may be unprofitable in the bulk liquid. May be it is simply unprofitable to stay near the surface. So, one can see the kinetic barrier which doesn't allow to attain the asymptotically leading channel.

Certainly, one can combine all mentioned possibilities and construct some new variants, where the rate of nucleation will differ from the ordinary classical theory.

1.3 Non stationarity of the fluctuation formation of the embryo

It is evident that in the theoretical description of the nucleation there exists at least two principal unsolvable problems - the fluctuations of thermodynamic variables and the unequivalency of the ensembles. The unequivalency of ensembles leads to the unequivalency of the additive thermodynamic values [10] of the order $\ln N$, where N is the number of the molecules in the system. As far as the rate of nucleation is proportional in the leading term to the exponential term, the error due to unequivalence of ensembles leads to the renormalization of the nucleation rate in N^{ε} times where ε is the coefficient of proportionality[10]. To determine the type of ensemble one has to add some generally unknown information about the embryo.

The fluctuations of additive values are rather small but only in the relative sense. The concrete split on the subsystems leads to the violation of this variable of the order[11] $\sqrt{N}$. So the exponent of this value has the giant variations.

It seems that this consideration is absolutely sufficient to close the problem. But one can notice two important facts. The first one is that

[9] It is difficult to rotate the molecule in the liquid.

[10] More rigorously there is some evident compensation of the bulk and the surface terms. It leads to some compensation of unequivalency of ensembles.

[11] Due to the Gibbs theorem there is also some compensation in the fluctuation effects.

the deviation in the rate of nucleation is very big. It can be hardly explained by the mentioned effects. One can also mention the specific qualitative behavior of this deviation.

Let us extract the specific behavior of J_{th}/J_{exp}.

- Theoretical value is greater than the experimental one.
- The mentioned value depends on the supersaturation weakly.
- This value grows with the growth of the temperature. The logarithm of this value is the smooth function of the temperature.

One has to give at least the qualitative explanation of these features.

Even the first feature is very important. Really, the construction of the free energy on the plane of the variables of description means that one has found the way to overcome the barrier. The introduction of the new variable leads to the mew may be more low way to the overcome the barrier. In any case the estimate from above is presented[12]. But the real value corresponds to more high value of barrier. The contradiction is evident.

The reason of the contradiction is the following. In the classical theory of nucleation it is assumed without any justifications that the way from the molecule of the vapor to the critical embryo is the equilibrium way. But there are no justification of such equilibrium. This is the unique reason (as this is stated by thermodynamic due to the sense of the minimal work) to increase the free energy.

Consider the analytical expansion of the expression for the free energy as the function of the size (of the number ν of the molecules inside the embryo). It means that the probability to eject the molecule by the given embryo doesn't depend on the state of the embryo but only by the internal state of the embryo. In the capillarity approximation this dependence is given by the known classical formula for the free energy obtained without any discussions about the unequilibrium state of the embryo.

In some rough approximation the whole region of the numbers of the molecules of the precritical embryo can be split into the two subregions. The critical embryo is in the equilibrium with the vapor. In the critical region the derivative of the free energy on the size of the embryo is small and one can speak about the approximate equilibrium. This region can

[12]The situation of the post critical barriers will be discussed later.

be spread until the values of ν where

$$dF/d\nu \sim d,$$

and d is some parameter[13] approximately equal to 1. Using the explicit expression for the free energy in the capillarity approximation one can get

$$a\frac{2}{3}\nu_0^{-1/3} - b = d$$

for the boundary ν_0 of the quasi equilibrium region. Note that the validity of the capillarity approximation requires

$$\frac{2a}{3b} \gg 1,$$

which put the restrictions for the maximal value of the supersaturation. In the determination of ν_0 this allows to neglect b in comparison with d taking into account that a isn't too big[14]. So, the value of ν_0 depends weakly on the supersaturation of the vapor.

The region with ν less than ν_0 is the essentially unequilibrium one. The state of equilibrium can be attained there only by the variation of the vapor density. Then one has to fulfill the additional work which depends on the size of this region. The sizes of this region are rather big - there must be at least ν_0 molecules of the vapor. Then this additional work has to be included in the free energy of the embryo formation. It is impossible to chose one molecule, compress it and put it inside the embryo by the equilibrium way.

So, one can see that the embryo overcomes the region of small ν (less than ν_0) by the unequilibrium way. It leads to the increase of the free energy necessary to overcome the activation barrier.

After the embryo has been formed one can suppose to return the additional work to the system. But it changes nothing[15] because we are interested in the amplitude of the free energy.

The description of the evolution in this unequilibrium region has to take into account some kinetic models of the embryo growth. This problem is very difficult and one can give here only some estimates.

As far as in the region of the small sizes

$$dF/d\nu \gg 1,$$

[13] More precisely one has to put q to some value which corresponds to the situation where the equibrium state of the embryo is violated.

[14] Ordinary $a \leq 10$

[15] It can lead to the heating of the embryo which is dangerous.

then the probability W^- to eject the molecule is many times greater than the probability W^+ of adsorption of the molecule. The embryo start the evolution from one molecule and then all other molecules are adsorbed. Denote via P_0 the probability of formation of the embryo of the size ν_0 if there were no acts of ejecting the molecules, but only the sequential adsorption of the molecules. Introduce the characteristic time t_0 of formation of the embryo by this way. Estimate the probability P_1 of formation of the embryo when it has ejected one molecule during the period of formation. Then it is necessary to add one molecule more and the time of formation t_1 increases

$$t_1 = t_0 + 1/W^+.$$

The fact that the embryo is formed longer leads to the increase of the probability to eject one molecule more. This probability is equal to the additional time multiplied by the intensity of the ejection, i.e. W^-/W^+ and[16] as the result the probability will be

$$P_1 = P_0 W^+/W^-,$$

which is many times less than P_0. So, the embryo has to grow rapidly without any ejection of the molecules.

The same considerations can be generalized for the case of the ejection of some big quantity of the molecules[17]. The main effect is due to the formation of the embryo without any ejection. Really, in these estimates the dependence W^- on ν has not been taken into account. This simplifies the consideration, but the result has only the qualitative sense.

To gather the molecules quickly one has to have them near the center of the embryo. To make this one has to compress the gas of ν_0 molecules until some fixed volume V. The size of this volume can be estimated on the base of the gas kinetic theory as

$$V^{1/3} \sim W^- v_t \nu_0,$$

where v_t is the heat velocity of the molecules. This volume ensures the possibility to construct the embryo of the size ν_0 more quickly than the embryo ejects the molecule of the vapor. Then the work of compression can be presented[18] in the following form

$$F_1 \sim \nu_0 \ln(\frac{v_v \nu_0}{V}),$$

[16] One has to calculate approximately the sum of the geometric progression.
[17] One has to calculate these values for the vapor in the neigborhood of the embryo.
[18] About the possibility of variation of F_1 and P/P_0 see later.

where v_v is the mean volume for the molecule in the vapor. As far as the ratio of the volumes is the argument of the logarithm, the dependence on the concrete value of the volume as the function of the number of the molecules is rather weak.

Note that the creation of the vapor with the other density requires the minimal work with the some functional form but with some other parameters.

The probability of formation of the critical embryo P_{tot} can be presented as the product of the probability to overcome the unequilibrium region P_0 and the probability to transform from the state with ν_0 molecules into the state with ν_c molecules. Namely,

$$P_{tot} = P_0 P(\nu_0 \to \nu_c).$$

To calculate $P(\nu_0 \to \nu_c)$ one can use the free energy in the capillary approximation and come to

$$P(\nu_0 \to \nu_c) = \exp(-F_c + F(\nu_0)).$$

The main dependence on the supersaturation is accumulated in $\exp(-F_c)$. It allows to present the last expression as

$$P(\nu_0 \to \nu_c) = const \ \exp(-F_c),$$

where the constant in front of exponent plays the role of the normalizing factor.

Determine the concrete value of ν_0. The calculations give

$$\nu_0 = (\frac{2a}{3d})^3.$$

The the rate of nucleation J in the leading order is equal to

$$J \sim const \exp(-F_c) \exp(-const(\frac{2a}{3d})^3 \ln(\frac{v_v \nu_0}{V})).$$

One can neglect the weak dependence in the logarithm[19]. Then for the ratio of the rates of nucleation one can get

$$J/J_{th} \sim const \exp(-a^3 const) < 1$$

[19]In the process of the derivation some unjustified propositions for the volumes of compression were made. The question "Why the small probability can not be compensated by the additional work?" was without the answer. Now these volumes disappear from the final formulas.

When the temperature increases then the surface tension decreases and absolute value of the renormalization in the last formula decreases.

The last formula satisfies to all features mentioned above. The possible increase of the nucleation rate can occur due to the consideration of some intensive parameters of the embryo description.

It is necessary to stress that the position and all characteristics of the critical embryo remain unperturbed. So, there is no contradiction between this theory and the thermodynamics.

* * *

In the further consideration only the specific exponential approximation will be necessary. It means that the rate of nucleation can be approximately presented as proportional to the exponent with the argument as the linear function of the supersaturation. This approximation must be valid at the variations of the supersaturation corresponding to the change of the stationary rate in few $(2 \div 3)$ times.

One can easily check that the free energy of the critical embryo in the capillarity approach leads to the mentioned approximation. One can also see that all reconsiderations mentioned in the previous two sections also allow such approximation. The same fact will be valid for all further reconsiderations of the stationary rate presented in this manuscript. It can be shown by the simple calculation and no special attention will be paid to this fact in the further constructions.

1.4 The hidden kinetic parameters

To describe the evolution of the hidden kinetic parameters one can use the methods from the binary theory of the nucleation. The multi component mixtures allow to vary many parameters of the condensated substance [11].

On the other hand there exists such specific difficulties as the Wilemski-Renninger paradox [12]. Now some new theoretical investigations of the binary condensation [13] appeared.

To see the analogy with the hidden kinetic parameters one can note that every embryo have to be described with the help of many intensive parameters[20]. May be some of them are rapid. So, the problem to describe the evolution in the multidimensional space of the embryo characteristics appears. This problem was solved in frames of the binary nucleation.

[20] The real number is unknown.

The classical binary theory of the condensation was constructed by Reiss [14]. But until the paper of [15] it was supposed that the transition occurs along the steepens descent line. In the cited paper Stauffer postulated some direction of the transition and found this direction. It was not clear why the phase transition must have one and the same direction in whole critical region. Only with the help of the Lorenz transformation one can justify this fact in the square approximation of the free energy near the saddle point [16].

Another problem was the enrichment of the surface layer by one of components which leads to the Gibbs adsorption equation. As the result the functional form of the free energy must be reconsidered. Particularly the expressions for the second derivatives at the saddle point have to be reconsidered with the help of the excess quantities in the surface layers.

As far as we are going to get the strong inequalities it is possible to ignore these reconsiderations[21]. The weak restriction is that the derivatives of the excess on the concentration aren't the leading terms in comparison with the bulk derivatives.

1.4.1 Thermodynamic hierarchy of variables

As far as we are seeking only for some estimates, in this subsection it will be sufficient to use for the free energy F of the formation of the embryo of ν_1 first component molecules and of ν_2 second component molecules the following expression in the capillarity approximation $F = \nu^{2/3} - B\nu$. Here ν is dimensionless surface energy in power $3/2$, B is the effective excess of the chemical potential. The value B depends on solution concentration ξ. The scale of variation of ν coincides with the scale of variation of the number of the molecules of some component in the embryo. The existence of the big value of this parameter is required by the thermodynamics.

The mentioned form of the free energy was described in [5] where it was the base of some topological statements. The hierarchy of the halfwidths was not observed in the mentioned paper.

To determine the characteristic scales of the halfwidths of the critical region one has to calculate the second derivatives at the saddle point

$$(\frac{\partial^2 F}{\partial \nu^2})_c = -\frac{2}{9}\nu_c^{-4/3},$$

[21] Taking into account these reconsiderations one can reproduce all presented constructions.

$$(\frac{\partial^2 F}{\partial \xi^2})_c = -\nu_c \frac{d^2 B(\xi)}{d\xi^2} \mid_{\xi=\xi_c},$$

$$(\frac{\partial^2 F}{\partial \xi \partial \nu})_c = -\frac{dB(\xi)}{d\xi} \mid_{\xi=\xi_c} .$$

It can be seen that the derivatives are proportional to the powers of the big parameter[22] ν_a.

So, the critical region is spread along ν and compressed along ξ. The ratio of the halfwidths has the scale $\nu_c^{1/6}$.

This hierarchy doesn't based on the definition of the critical point. So, it will take place even with the Gibbs adsorption equation taken into account.

This hierarchy[23] is quite natural for the rapid variables of the embryo description. Ordinary the relaxation time is many times less than the characteristic time of the evolution along the unstable variable (which is the quasi integral)[24].

We shall call this parameter as the kinetic parameter. All such parameters are are supposed to be rapid.

1.4.2 Kinetic equation

Introduce the Reiss variables x, y as the variables when the free energy in the critical region has the form

$$F = F_c - x^2 + y^2,$$

where F_c is the free energy in the saddle point. These variables can be obtained from ν_1, ν_2 by rotation and rescaling[25].

[22]The value of ν_{1c} and ν_{2c} are also the big parameters to use the approximation of the homogeneous solution inside the embryo.

[23]The scales must be chosen to have one and the same order of the flows along these axis.

[24]The opposite situation corresponds to the condensation on some set of the heterogeneous centers with the different activities. We have the set of the separate activation barriers with the different heights for the different values of the stable characteristic of the variable which parameterizes this set. The definition of the stationary flow is absolutely analogous to the case of one variable, the value of the intensive variable here is some external parameter. An interaction occurs in the further evolution which can be described analogously to the forth chapter.

[25]May be some part of the Lorenz transformation with an arbitrary parameter has been made. So, these variables aren't completely fixed.

Instead of rotation and rescaling it is more convenient to introduce the separated variables directly. The variables ν, ξ are the stable and unstable ones. When one neglects the surface excesses one can come to

$$\frac{\partial^2 F}{\partial \xi \partial \nu} = -\frac{dB(\xi)}{d\xi},$$

which is vanished in the saddle point.

In the Fokker-Planck approximation the kinetic equation for the distribution function n can be written in the following form

$$\partial_t n(\nu_1, \nu_2) = W_1 \partial_1 [n\partial_1 F + \partial_1 n] + W_2 \partial_2 [n\partial_2 F + \partial_2 n],$$

where W_1, W_2 are the kinetic coefficients, i.e. the numbers of the first sort molecules and the second sort molecules which are adsorbed by the embryo in the unit of time. The differentiation on the number of the molecules of the given sort in marked by the index near the symbol of the partial differentiation.

In x, y the kinetic equation has the following form:

$$\partial_t n(\nu_1, \nu_2) = R[\partial_x [n\partial_x F + \partial_x n] - k^{-1}[\partial_x [n\partial_y F + \partial_y n] + \partial_y [n\partial_x F + \partial_x n]]$$
$$+k^{-2} q \partial_y [n\partial_y F + \partial_y n]]$$

with the small parameter k. The value of R isn't important because it can be changed by the time rescaling. The scale of q is arbitrary.

The variables x, y can be obtained from ν_1, ν_2 by the linear transformation

$$x = c_{11}(\nu_1 - \nu_{1c}) + c_{12}(\nu_2 - \nu_{2c}),$$
$$y = c_{21}(\nu_1 - \nu_{1c}) + c_{22}(\nu_2 - \nu_{2c})$$

(which isn't orthogonal) with the known coefficients

$$c_{11} = [-\frac{1}{2}(\frac{\partial^2 F}{\partial \nu^2})_c]^{1/2} (\frac{\partial \nu}{\partial \nu_1})_c \sim \nu_c^{-2/3},$$

$$c_{12} = [-\frac{1}{2}(\frac{\partial^2 F}{\partial \nu^2})_c]^{1/2} (\frac{\partial \nu}{\partial \nu_2})_c \sim \nu_c^{-2/3},$$

$$c_{21} = [\frac{1}{2}(\frac{\partial^2 F}{\partial \xi^2})_c]^{1/2} (\frac{\partial \xi}{\partial \nu_1})_c \sim \nu_c^{-1/2},$$

$$c_{22} = [\frac{1}{2}(\frac{\partial^2 F}{\partial \xi^2})_c]^{1/2} (\frac{\partial \xi}{\partial \nu_2})_c \sim \nu_c^{-1/2}.$$

For R, k, q one can get the following expressions

$$R = W_1 c_{11}^2 + W_2 c_{12}^2,$$

$$k = -\frac{W_1 c_{11}^2 + W_2 c_{12}^2}{W_1 c_{11} c_{21} + W_2 c_{12} c_{22}},$$

$$q = 1 + W_1 W_2 (\frac{c_{11} c_{22} - c_{12} c_{21}}{W_1 c_{11} c_{21} + W_2 c_{12} c_{22}})^2.$$

The plausible but not rigorous consideration by Reiss is the following one. The main operator of kinetic equation is the last term in r.h.s. It ensures the relaxation over the stable variable and the kinetic equation becomes the one dimensional one. The consideration of the evolution only over the unstable variable leads to the reduction of the kinetic equation to

$$\partial_t n(\nu_1, \nu_2) = R \partial_x [n \partial_x F + \partial_x n]$$

The solution of the last equation leads to the results of Reiss. But in the cited paper of Reiss the hierarchy was not observed.

But in the case of the hidden parameter the solution of Reiss is absolutely natural. One can not assume the relaxation of the rapid hidden variable.

1.4.3 The influence on the characteristics of the process

Introduce the Lorenz transformation via formulas

$$\psi = \frac{x + \alpha y}{\sqrt{1 - \alpha^2}}, \qquad \eta = \frac{y + \alpha x}{\sqrt{1 - \alpha^2}},$$

which conserves the form of the free energy in the critical region.

The kinetic equation transforms to

$$\partial_t n(\nu_1, \nu_2) = R(1 - \alpha^2)^{-1} k^{-2} [[(k - \alpha)^2 + \alpha^2 (q - 1)] \partial_\psi [n \partial_\psi F + \partial_\psi n] -$$

$$[(k - \alpha)(1 - k\alpha) - \alpha(q - 1)][\partial_\psi [n \partial_\eta F + \partial_\eta n] +$$

$$\partial_\eta [n \partial_\psi F + \partial_\psi n]] + [(1 - k\alpha)^2 + q - 1] \partial_\eta [n \partial_\eta F + \partial_\eta n]].$$

Parameter α which has the absolute value less than 1 has to be chosen to vanish the cross term. Then

$$\partial_t n(\nu_1, \nu_2) = A \partial_\psi [n \partial_\psi F + \partial_\psi n] + C \partial_\eta [n \partial_\eta F + \partial_\eta n]$$

$$= \frac{R}{k^2}(1-\alpha^2)^{-1}[(1-k\alpha)^2 + \frac{(k-\alpha)(1-k\alpha)}{\alpha}],$$

$$A = \frac{R}{k^2}(1-\alpha^2)^{-1}[(k-\alpha)^2 + \alpha(k-\alpha)(1-k\alpha)].$$

The parameter of the Lorenz transformation is given by

$$\alpha = \frac{1}{2k}[k^2 + q - \sqrt{(k^2+q)^2 - 4k^2}].$$

After the decomposition one can come to

$$\alpha = \frac{1}{q}k.$$

One can see that it is small. So, it is difficult to see the hidden kinetic parameter.

But the leading term for A

$$A = R\frac{q-1}{q}.$$

isn't small. So the correction to the Reiss formula is essential.

As the result one can see the hidden character of the rapid variable.

Some consequences for the binary nucleation

Let us extract the conditions when A essentially differs from R. It can be only when q is near the unity.

In the derivation of the expression for q no suppositions about W_1 and W_2 have been made. As far as $\frac{\partial\xi}{\partial\nu_1} = \frac{\partial(1-\xi)}{\partial\nu_2} = -\frac{\partial\xi}{\partial\nu_2}$ the value of q can be near the unity only when $W_1 \ll W_2$, $W_1 \gg W_2$. Namely, this situation occurs when there is the rapid component. *The essential variation of the nucleation rate in comparison with the Reiss formula is possible only under the hierarchy of the kinetic coefficients.* Later it will be shown that in this situation it is possible that the transition occurs far from the saddle point (see chapter 3).

Also one has to analyze the situation of the small concentrations as far as $\xi \sim 1-\xi$ has been taken into account. It will be done in the third chapter.

Under the hierarchy one have the evident rapid component and the analysis can be simplified.

The simplification can be made also directly in the final formulas and the expression for A

$$A = W_2\frac{(c_{11}c_{22} - c_{12}c_{21})^2}{c_{21}^2}$$

is proportional to W_2. Then

$$A = W_2(-\frac{1}{2}\frac{\partial^2 F}{\partial \nu^2})[\frac{\partial \nu}{\partial \nu_1} + \frac{\partial \nu}{\partial \nu_2}]^2$$

with the evident physical interpretation.

In the further considerations of this section this simplification isn't used.

1.4.4 Kinetic equation in the post critical region

In the post critical region one can assume the derivative on the unstable variable to be the local constant and reduce the kinetic equation to

$$\partial_t n = R[\partial_x(\partial_x + h) - k^{-1}(\partial_x(\partial_y + 2y) + \partial_y(\partial_x + h)) + k^{-2}q\partial_y(\partial_y + 2y)]n,$$

where h is the constant coefficient corresponding to the first derivative on the unstable variable and the values of R,k, q are changed as far as the derivatives are taken now in the local current point. Renormalize the scale over the unstable variable as to put $h = 1$. The hierarchy remains unperturbed.

We are interested in the stationary solution and shall seek it in the form

$$n = P(x)\exp(-(y - y_0)^2)$$

with the constant mean value y_0 and some function $P(x)$. The dependence $P(x)$ is rather weak and can be neglected. For y_0 one can get taking into account

$$\partial_y \exp(-(y - y_0)^2) = -2(y - y_0)\exp(-(y - y_0)^2),$$

$$\partial_y(\partial_y + 2y)\exp(-(y - y_0)^2) = -4y_0(y - y_0)\exp(-(y - y_0)^2)$$

the following relation

$$\frac{kh}{q} = 2y_0.$$

So the solution is obtained[26]. We see that the deviation of the rapid parameter is small also in the post critical region and the hidden parameter can not be extracted.

[26]It is the limit of the relaxation of the true solution. In the third chapter it will be shown that this is the estimate from above for the region of the localization of the solution.

Due to the slope of the free energy surface on ν the minimum of the free energy in the cross section depends on the slope of this cross section. But as far as the slope of the free energy surface on ν is small the deviation of the minimum is small also. This deviation can be considered as the deviation of the mean value of the rapid variable and leads to the absence of the possibility to extract this variable in the post critical region also.

The analogous way can be applied also for the critical region. In the critical region one can make the substitution

$$n = P(x)\exp(-(y - y_0(x))^2),$$

where y_0 is now the function of x. The determination of y_0 is given by

$$(\partial_x - 2x)n = -J_x,$$

there the r.h.s. is constant. Then

$$\partial_x n = -J_x + 2xn.$$

The linear character of the last equation ensures the linear dependence of y_0 on the unstable variable. As far as the flow is reciprocal to the halfwidht (along the trajectory y_0) one can get the equation on the flow. The linear dependence of y_0 on x ensure the linear character of the transformation which is analogous to the Lorenz transformation.

This way of considerations can be apply to the more general situations without the square form of the free energy. Now the trajectory isn't the straight line and the solution is some approximation based on the hierarchy.

Another problem to be solved is the definition of the kinetic coefficient. Only in the case of the binary condensation these coefficients have the explicit definition. When the parameter is hidden the kinetic coefficient is unknown and can be determined only from the rate of nucleation.

When the deviation of the flow from the steepens descent situation is essential there is the danger to violate the square form of the free energy. The boundary conditions for kinetic equation in the critical region are the following

$$n/n^e = 1 \qquad x \ll -1 \qquad -\infty < y < \infty,$$

$$n/n^e = 0 \qquad x \gg 1 \qquad -\infty < y < \infty$$

and in reality they have to be observed at

$$n/n^e = 1 \qquad x \sim -1 \qquad -1 < y < 1,$$

$$n/n^e = 0 \qquad x \sim 1 \qquad -1 < y < 1.$$

After the Lorenz transformation

$$n/n^e = 1 \qquad \psi \sim -1 \qquad -1 < \eta < 1,$$

$$n/n^e = 0 \qquad \psi \sim 1 \qquad -1 < \eta < 1.$$

When the deviation of the nucleation rate from the steepens descent approach is essential the critical region is stretched along one of the lines $F = F_c$ where the transition occurs. The square approximation in such stretched region is probably invalid. Then one has to use the methods described in the third chapter.

Now we are going to present some constructive ideas to show the internal resources of the classical expression for the free energy

1.5 Theoretical description of the nucleation of alcanes

Despite the serious problems in the experimental investigations the evident progress was achieved in the last years by Katz in the experiments of the alcanes nucleation. The results were organized in the interpolation formula [22]. So, now it is possible to give the theoretical derivation of this formula.

1.5.1 Katz formula

It is more convenient to rewrite the interpolation Kats formula as the expression for the free energy F of the embryo of ν molecules $F = a\nu^{2/3} - b\nu$ where b is the excess of the chemical potential and a doesn't coincide with the classical dimensionless surface tension but is determined by the following expression

$$a = a_\infty(1 - \frac{\delta}{r}). \tag{1.5.1}$$

In the last expression the parameter a_∞ is the classical value of the dimensionless surface tension of the plane surface, r is the radius of the embryo, δ is some parameter of interpolation.

According to Tolmen [23] the value of δ can be interpreted as the distance between the equimolecular surface and the surface of tension [24].

The interpolation for δ as the function of the supersaturation and the temperature has the following form

$$\delta = 0.25[nm] - 0.68[nm]\frac{T}{T_c},$$

where T_c is the second order phase transition temperature[27]. The dependence of the supersaturation is absent.

One has to make the following comments:

- As far as this is the linear interpolation we shall seek the expression in the linear form.
- The mentioned expression is checked only for some rather low temperatures.
- In the mentioned interval of the temperatures the theoretical nucleation rate is greater than the experimental rate.

One can present δ as the superposition of the effects from the different physical effects

$$\delta = \sum_i \delta_i$$

1.5.2 Asymmetric barriers

The capillarity approximation consider the spherical embryo. It is possible only when the number of the molecules is equal to the magic number. The magic number corresponds to the dense occupation of the sphere with the integer diameter by the molecules. From the first point of view it seems that the rate of nucleation must have some singularities at the magic numbers. It can not be observed in experiments. The reason is that the increase of the free energy due to the deviation of the number of the molecules from the magic one is greater than the decrease of the free energy in the capillarity approximation by the deviation from the critical embryo.

[27] The distances are taken in nanometers.

In the capillarity approximation for F one can get for the width $\bar{\Delta}\nu$ of the critical region the following expression

$$\bar{\Delta}\nu = \frac{3}{\sqrt{a}}\nu_c^{2/3}.$$

This expression has the same order as the number $3\nu^{2/3}$ of the molecules in the surface layer of the embryo. So in the critical region the embryo transforms from one magic number to another and pass through all possible specific situations and there is no sharp dependence on the magic numbers of the molecules in the critical embryo.

Consider the embryo with the magic number. Add a few molecules. When the temperature is low then the surface of tension can has the curved form. The reason is that a_∞ is great and the correction term (due to the curvature) can not be relatively essential. Then

$$\delta_1(T \ll T_c) = 0.$$

When the temperature is near T_c than the surface tension is small and the curvature corrections of the surface tension is the leading term. So the tension of surface has to be drawn with minimum of curvature. Then it must be replaced immediately on the next layer of the embryo.

To get the rate of nucleation (in the leading term) one has to calculate the maximum of the free energy in the most asymmetric case[28]. Then

$$\delta_1(T_c) = D,$$

where D is the diameter of the molecule.

After the linear interpolation one can come to

$$\delta_1 = D\frac{T}{T_c}.$$

1.5.3 The excess of the surface energy in the vapor

As far as we are interested in the behavior at the low temperatures then one can add the effects despite the fact that at $T = T_c$ there will be some problems.

For further considerations one has to notice that n-alcane molecules are the long cylinders and every cross section has one carbon atom between two atoms of hydrogen.

[28] Certainly, the steepens descent method can not be applied but we need only the leading exponential term.

Analyze the position of the surface of tension with respect to the molecule in the surface layer. When the temperature is low then it is profitable to put it most close to the center of the embryo, i.e. on the atom of hydrogen which is close to the center of the embryo. Then

$$\delta_2(T \ll T_c) = -2|CH| - |H|,$$

where $|H|$ is the size of the atom of the hydrogen (Bohr radius), $|CH|$ is the length of the bound between the carbon and the hydrogen, one can can take the value of the free radical CH.

When the temperature is close to the critical one then the difference between the vapor and the liquid phase isn't too big. Then the same conclusions have to be fulfilled also for the vapor and

$$\delta_2(T = T_c) = 0.$$

The linear interpolation leads to

$$\delta_2 = (-2|CH| - |H|) + (2|CH| + |H|)\frac{T}{T_c}.$$

1.5.4 Numerical results

As the diameter of the molecule one can take

$$D = 2|CH| + 2|H|.$$

For the superposition we have

$$\delta = -2|CH| - |H| + (4|CH| + 3|H|)\frac{T}{T_c}.$$

With the concrete values $|CH| = 0.112[nm]$, $|H| = 0.053[nm]$, one can get

$$\delta = 0.277[nm] - 0.613[nm]\frac{T}{T_c}.$$

This expression practically coincides with the Katz interpolation formula.

The formal generalization for the other substances is obvious.

Chapter 2

Nucleation in the dynamic conditions

2.1 Process of the homogeneous condensation under the continuous action of the external conditions

The process of condensation is initiated by the external conditions. Ordinary they have the smooth character and continue the variation after the beginning of the phase transformation. We shall call such conditions as the dynamic ones. The following theory will describe the condensation under the dynamic conditions in the macroscopic description of the critical embryo.

The following model of calculations will be adopted

- The system is homogeneous in space.
- All heterogeneous centers have one and the same nature.
- The total number of the heterogeneous centers is fixed.
- The regime of the substance exchange is the free molecular one.
- There are no thermal effects.

We consider the system of the unit initial volume.

2.1.1 External supersaturation

The total number of the molecules is n_{tot}, the total number of the heterogeneous centers is η_{tot}. The values η_{tot} and n_{tot} are the known functions of time. The relation between the supersaturation and the temperature is given by the Klapeiron-Klausius equation

$$n_\infty(T) = n_\infty(T_*)\exp[\beta\frac{T-T_*}{T_*}] \quad , \qquad \frac{T}{T_*} \approx (\frac{n_{\infty\,*}}{n_\infty})^{-1/\beta} \quad , \qquad (2.1.1)$$

where β is the heat of condensation of one molecule and index "$*$" denotes the moment t_*. As far as t_* is the basic point in the approximations the choice of t_* will lead to the concrete error. The moment t_* can be chosen to minimize the error approximately as the moment when the half of the total number of the droplets is formed.

The power of metastability can be characterized by the value of the supersaturation. Often instead of the definition given in the first chapter the following definition

$$\zeta = \frac{n}{n_\infty} \qquad (2.1.2)$$

is used. One can use use both definitions except the paragraphs of the third chapter devoted to the coordination of the power laws for the different components. We shall not mention this specially. The value of the ideal supersaturation is introduced by

$$\Phi = \frac{n_{tot}}{n_\infty} \quad . \qquad (2.1.3)$$

The definition of the ideal supersaturation have to be coordinated with the definition of the real supersaturation.

The value of the ideal supersaturation can be reduced by the consumption of the vapor by the equilibrium embryos. The ideal supersaturation has to be changed by the external supersaturation

$$\Omega = \frac{1}{n_\infty}(n_{tot} - \eta_{tot}\nu_e\,|_{\zeta=\Omega}) \quad . \qquad (2.1.4)$$

The last equation gives the self consistent definition of Ω. Due to the weak dependence of ν_e on Ω this equation can be solved by iterations. The first iteration

$$\Omega = \frac{1}{n_\infty}(n_{tot} - \eta_{tot}\nu_e\,|_{\zeta=\Phi}) \qquad (2.1.5)$$

is absolutely sufficient. The behavior of Ω resembles the behavior of Φ. It is smooth in time.

In the further consideration we shall call external supersaturation as the ideal one.

2.1.2 Condensation kinetics equations

The wide class of the laws of growth is described by the power like dependencies[1]

$$d\nu/dt \sim \nu^{1-\alpha}\varphi(t)/\alpha \quad ,$$

where $\varphi(t)$ is some rather smooth function of time. Then the variable

$$\rho = \nu^{\alpha} \tag{2.1.6}$$

grows with the velocity which doesn't depend on the value of the variable.

The procedure presented here can be applied for the arbitrary positive $\alpha \leq 1$. When $\alpha = 1$ the system of the condensation equations can be solved analytically. We suppose that $1 - \alpha$ isn't too small in comparison with unity[2].

Formulate two suppositions which will be justified later. The first states that the leading role in the vapor consumption is played by the super critical embryos, i.e. by the droplets. Then the characteristic scale ρ_1 of the embryo essentially exceeds ρ_c

$$\rho_1 \gg \rho_c \quad . \tag{2.1.7}$$

Then one can consider only the regular growth of the embryos and put the initial size of the droplet to the zero. Then the kinetic equation[3] for the distribution $p(\rho, t)$ transforms to

$$\frac{\partial}{\partial t}p(\rho,t) = -\frac{\partial}{\partial t}[p(\rho,t)\frac{d\rho}{dt}] \quad . \tag{2.1.8}$$

The solution has to be multiplied by $\Theta\{\Theta(\rho \geq 0) = 1, \Theta(\rho < 0) = 0\}$. So, for the distribution $p(\rho, t)$ of the droplets over ρ one can get

$$p(\rho,t) = \frac{n_{\infty *}V_*}{n_\infty V}\Theta(z-x)f(x) \quad , \tag{2.1.9}$$

[1] As far as we shall use the results of this section later the generalized law of growth will be considered.

[2] In this case one can act in frames of the perturbation theory.

[3] In the unit volume in units of n_∞.

where f is some function of the argument

$$x = z - \rho \quad , \tag{2.1.10}$$

z is the coordinate ρ of the droplet formed at $t = t_*$, V is the volume of the system. Then the function z can be obtained from

$$\frac{dz}{dt} = \frac{d\rho}{dt} \equiv \varphi(t) \quad , \tag{2.1.11}$$

$$z \mid_{t=t_*} = 0 \quad . \tag{2.1.12}$$

The form of $f(x)$ has to be established from the boundary condition. It will be called as the spectrum.

To establish the boundary condition one has to use the second supposition which states that the state of the embryos in the near critical region is described by the quasi stationary distribution function $f_s(\zeta)\eta/n_\infty$, where the dependence on η is extracted explicitly. The classical nucleation theory gives for the stationary distribution function the following expression[4]

$$f_s \sim \frac{K \exp(-\Delta F)}{\Delta\nu_e \Delta\nu_c \varphi(t)} \quad , \tag{2.1.13}$$

where K is the known kinetic factor.

The second supposition has to be observed during the period of the intensive formation of the new embryos. Let t_ζ be the characteristic time of the variation in the critical region and t_s be the time of relaxation to the stationary state in the critical region. The necessary requirement can be written as the following one

$$t_\zeta \gg t_s \quad . \tag{2.1.14}$$

The last two inequalities will be valid in all situations except the case when all heterogeneous centers become the centers of the droplets. But in this situation the result is the evident and the evolution is simple.

As $f_s(\zeta)\eta/n_\infty$ is the boundary condition at $\rho = 0$ one can get for $f(x)$ the following expression

$$f(x) = f_s(\zeta) \mid_{\zeta=\zeta(x)} \frac{\eta(x)}{n_\infty} \quad . \tag{2.1.15}$$

[4]For the generalized law growth.

To establish the form of the functions $\zeta(x)$ and $\eta(x)$ it is necessary to introduce the equations of the balance of the heterogeneous centers and of the condensated substance

$$\Omega = \zeta + g \quad , \qquad g(z) = \frac{n_\infty \, {}_*V_*}{n_\infty V} \int_{-\infty}^{z} dx (z-x)^{1/\alpha} f(x) \quad , \tag{2.1.16}$$

$$\eta_{tot} = \eta + N \quad , \qquad N(z) = \frac{n_\infty \, {}_*V_*}{V} \int_{-\infty}^{z} dx f(x) \quad . \tag{2.1.17}$$

The first equation is written in the simplification of the collective consumption of the vapor. It means that the embryo consumes the vapor homogeneously from the whole volume. It will be corrected in the next chapters.

2.1.3 Some approximations

Introduce some parameter Γ

$$\Gamma = -\Omega_* \frac{d\Delta F(\zeta)}{d\zeta} \mid_{\zeta=\Omega_*} \quad . \tag{2.1.18}$$

Due to

$$\Gamma = \nu_c(\Omega_*) - \nu_e(\Omega_*) \tag{2.1.19}$$

(may be it necessary to add $\zeta/(\zeta+1)$) in the macroscopic description one can get

$$\Gamma \gg 1 \quad . \tag{2.1.20}$$

For the majority of the external conditions one can get

$$\Gamma (\frac{d\Omega}{dx})^2 \gg \Omega \mid \frac{d^2\Omega}{dx^2} \mid \tag{2.1.21}$$

in the neighborhood of Ω_* due to the big value of Γ. This inequality extracts the class of dynamic conditions. The last equation allows to write the linear approximation for $\Omega(x)$ at the period of the intensive formation of the droplets (PIFD).

Due to (2.1.13), (2.1.15) the function $f(x)$ is the sharp function of ζ and of coordinate x. The exponential dependence is much more strong than $(z-x)^{1/\alpha}$ and the subintegral functions in (2.1.16), (2.1.17) are well localized in x. So, PIFD is well extracted. During this period the following inequalities

$$\frac{\Omega - \Omega_*}{\Omega_*} \leq \Gamma^{-1} \quad , \qquad \frac{\zeta - \Omega_*}{\Omega_*} \leq \Gamma^{-1} \tag{2.1.22}$$

are observed. These inequalities will appear automatically in the further considerations. From the last equation it follows

$$V \approx V_* \quad , \qquad n_\infty \approx n_{\infty\,*} \tag{2.1.23}$$

for PIFD. Due to (2.1.13), (2.1.15), (2.1.22) the following approximation is valid

$$f(x) = f_s \exp(\Gamma \frac{\zeta(x) - \Omega_*}{\Omega_*}) \frac{\eta(x)}{n_\infty} \quad , f_s = f_s(\Omega_*) \tag{2.1.24}$$

for PIFD. To justify the last approximation one has to take into account the following estimates

$$\frac{d\nu_c}{d\zeta} \sim \frac{d\nu_{c\ hom}}{d\zeta} \quad , \qquad \frac{d\nu_c}{d\zeta} - \frac{d\nu_e}{d\zeta} \sim \frac{d\nu_c}{d\zeta} \quad , \qquad \nu_c - \nu_e \sim \nu_c \quad , \tag{2.1.25}$$

where $\nu_{c\ hom}$ is the number of the molecules on the homogeneous critical embryo. So one can come to the strong inequality

$$| \frac{d\Delta F(\zeta)}{d\zeta} |^2 \gg | \frac{d^2 \Delta F(\zeta)}{d\zeta^2} | \quad , \tag{2.1.26}$$

which leads to the possibility of the linearization of ΔF. The most sharp dependence is given by $\exp(-\Delta F)$. This put some weak restrictions on $\varphi(t)$. Naturally, it is necessary to check this for the given sort of the heterogeneous centers.

The other important parameter c is defined as

$$c = \frac{\Gamma}{\Omega_*} \frac{d\Omega(x)}{dx} \mid_{x=0} \quad . \tag{2.1.27}$$

It is necessary for the linearization near $x = 0$ of the function $\Omega(x)$ at PIFD. After the linearization one can get with the help of (2.1.21):

$$\Omega(x) = \Omega_* + \frac{\Omega_* c x}{\Gamma} \quad . \tag{2.1.28}$$

This linearization is based on the strong inequality

$$(\frac{d\Omega}{dx})^2 \gg |\delta_1 \Omega| |\frac{d^2 \Omega}{dx^2}| \quad , \tag{2.1.29}$$

where $\delta_1 \Omega$ is the variation of the Ω during PIFD. Taking into account (2.1.22), one can see that the last equation can be reduced from (2.1.21) which leads to the following form of (2.1.16):

$$g(z) = f_s \int_{-\infty}^{z} dx (z - x)^{1/\alpha} \exp(cx - \Gamma \frac{g(x)}{\Omega_*}) \frac{\eta(x)}{n_{\infty\,*}} \quad . \tag{2.1.30}$$

The function $f(x)$ can be presented in the following form

$$f(x) = -\frac{d\eta(x)}{n_{\infty\ *}dx} \quad . \tag{2.1.31}$$

This differential equation can be integrated

$$\eta(z) = \eta(-\infty)\exp[-f_s\int_{-\infty}^{z} dx\exp(cx - \Gamma\frac{g(x)}{\Omega_*})] \quad . \tag{2.1.32}$$

The argument $-\infty$ marks the values at the beginning of PIFD and ∞ corresponds to the final of this period.

The total number of the droplets can be given by

$$N(x) = \eta(-\infty) - \eta(x) \tag{2.1.33}$$

and has the following integral representation

$$N(z) = \int_{-\infty}^{z} f(x)dxn_{\infty\ *} \quad . \tag{2.1.34}$$

2.1.4 The method of the disbalanced iterations

Denote the operator of the r.h.s. of (2.1.30) as $G(g(x), \eta(x))$ and the operator of the r.h.s. of (2.1.32) as $H(g(x))$. The disbalanced iterations[5] are constructed according to the following rule

$$g_{a\ (i+1)} = G(g_{a\ (i)}, \eta_{a\ (i)}) \quad , \qquad \eta_{a\ (i+1)} = H(g_{a\ (i)}) \quad . \tag{2.1.35}$$

When the initial approximation is $g_{a\ (0)} = 0, \eta_{a\ (0)} = \eta(-\infty)$ then we have the estimates from above and from below for the solution. The main property of the operators G and H are the monotonic character of these operators. If

$$g_p(x) \geq g_q(x)$$

for all values of the arguments then

$$H(g_p(x)) \geq H(g_q(x)) \tag{2.1.36}$$

for all values of x. If

$$g_p(x) \geq g_q(x) \qquad \eta_p \leq \eta_q$$

[5]Of the type "a".

for all values of arguments then

$$G(g_p(x), \eta_p(x)) \leq G(g_q(x), \eta_q(x)) \tag{2.1.37}$$

for all values of x.

From the last equations and the evident inequalities

$$g_{a\ (0)} \leq g \ , \quad g_{a\ (2)} \geq g_{a\ (0)} = 0 \ , \quad \eta \leq \eta_{a\ (0)} \ , \quad \eta_{a\ (2)} \leq \eta_{a\ (0)} = \eta(-\infty) \tag{2.1.38}$$

one can construct the following chains of the inequalities

$$g_{a\ (0)} \leq g_{a\ (2)} \leq ... \leq g_{a\ (2i)} \leq ... \leq g \tag{2.1.39}$$

$$\leq ... \leq g_{a\ (2i+1)} \leq ... \leq g_{a\ (3)} \leq g_{a\ (1)} \ ,$$

$$\eta_{a\ (0)} \geq \eta_{a\ (2)} \geq ... \geq \eta_{a\ (2i)} \geq ... \geq \eta \tag{2.1.40}$$

$$\geq ... \geq \eta_{a\ (2i+1)} \geq ... \geq \eta_{a\ (3)} \geq \eta_{a\ (1)} \ .$$

From the last equations it follows that $\{g_{a\ (2i)}\}$ and $\{\eta_{a\ (2i+1)}\}$ grow monotonically with the growth of the number. The opposite fact is valid for $\{g_{a\ (2i+1)}\}$ and $\{\eta_{a\ (2i)}\}$. So, the odd and the even iterations converge. To prove the existence and the uniqueness of the solution one can construct the new iterations $g_{b\ (i)}$ (reduced iterations) according to

$$g_{b\ (i+1)} = G(g_{b\ (i)}, H(g_i)) \ . \tag{2.1.41}$$

The initial approximation is chosen as $g_{b\ (0)} = 0$. These iterations differ from $g_{a\ (i)}, \eta_{a\ (i)}$.

The reduced iterations are rather more natural than the disbalanced ones. The substitution of the second equation in the first one is quite natural. It is more natural to speak about the special split of the common balance equation into two parts. This split is the main idea of the method the disbalanced iterations.

The iterations $g_{a\ (2i)}, g_{a\ (2i+1)}$ estimate the iterations $g_{b\ (i)}$:

$$g_{a\ (2i+1)} \geq g_{b\ (2i+1)} \ , \qquad g_{a\ (2i)} \leq g_{b\ (2i)} \ . \tag{2.1.42}$$

The equation (2.1.41) can be rewritten as

$$g_{b\ (i+1)} = \int_{-\infty}^{z} (z-x)^{1/\alpha} L(g_{b\ (i)}(x)) dx \ , \tag{2.1.43}$$

where the following function is extracted

$$L(g_i(z)) = f_s \frac{\eta(-\infty)}{n_{\infty\ *}} \exp(cx - \frac{\Gamma g_i(z)}{\Omega_*}) \exp(-f_* \int_{-\infty}^{z} \exp(cx - \frac{\Gamma g_i}{\Omega_*}) dx) \quad . \tag{2.1.44}$$

The next iteration (both reduced and disbalanced) is constructed on the base of the previous one with the argument less than z. Then the disbalanced second iteration gives the estimate from above for the region of the essential values of z. One can get the approximations for the number of the droplets and for the spectrum

$$N_{(i)}(z) = \eta(-\infty) - \eta_{(i)}(z) \quad , \tag{2.1.45}$$

$$f_{(i)} = -\frac{d\eta_{(i)}}{n_{\infty\ *} dz} \quad . \tag{2.1.46}$$

The last equation leads to

$$f_{(i)} = \frac{f_s}{n_\infty} \eta_{(i)}(z) \exp(cz - \Gamma \frac{g_{(i-1)}(z)}{\Omega_*}) \quad ,$$

which doesn't coincide with the spectrum in the expression for $g_{a\ (i)}$ in the disbalanced iterations

$$f_{p(i)} = \frac{f_s}{n_\infty} \eta_{a(i-1)} \exp(cz - \Gamma \frac{g_{(i-1)}(z)}{\Omega_*}) \quad ,$$

but coincide with the spectrum in the reduced iterations (the coincidence is the formal one). For $f_{p(i)}$ the following chain is valid

$$f_{p(1)}(x) \geq f_{p(3)}(x) \geq ... \geq f_{p(2i+1)}(x) \geq ... \geq f_p(x)$$

$$f_p(x) \geq ... \geq f_{p(2i)}(x) \geq ... \geq f_{p(4)}(x) \geq f_{p(2)}(x) \quad .$$

æ

In the second approximation

$$f_{a\ (2)}(x) = \frac{\eta(-\infty)}{n_{\infty\ *}} f_s \exp[cx - h f_s \frac{\exp(cx)}{c} - \frac{1 - \exp(-h f_s \frac{\exp(cx)}{c})}{h}] \quad , \tag{2.1.47}$$

$$\eta_{a\ (2)} = \eta(-\infty) \exp(-\frac{1 - \exp(-h f_s \frac{\exp(cz)}{c})}{h}) \quad , \tag{2.1.48}$$

$$N_{a\ (2)} = \eta(-\infty)[1 - \exp(-\frac{1 - \exp(-h f_s \frac{\exp(cx)}{c})}{h})] \quad , \tag{2.1.49}$$

where

$$h = \frac{\gamma(\frac{1}{\alpha})\Gamma\eta(-\infty)}{\Omega_* n_{\infty *} c^{1/\alpha}} \quad , \qquad \gamma(\frac{1}{\alpha}) = \int_0^\infty y^{1/\alpha} \exp(-y) dy \quad . \tag{2.1.50}$$

Iterations $N_{a\ (i)}$ satisfy the chains of inequalities

$$\begin{aligned} N_{a\ (2)} \leq N_{a\ (4)} \leq ... \leq N_{a\ (2i)} \leq ... \leq N \\ \leq ... N_{a\ (2i+1)} \leq ... \leq N_{a\ (3)} \leq N_{a\ (1)} \quad . \end{aligned} \tag{2.1.51}$$

The analysis of the expression for $f_{p(3)}(z)$ leads to the existence of the upper limit for the essential values of z. This boundary will be marked by the index "b". The analysis of the asymptotes $g(x)$ and $\eta(x)$ leads to the existence of the absolutely unessential region of the big negative z due to

1) inequalities

$$g(x) \geq 0 \quad , \quad \eta(x) \geq \eta_{a\ 2}(x) \quad , \quad \frac{d\eta}{dx} \leq 0 \quad , \quad \frac{dg}{dx} \geq 0 \quad ,$$

2) the explicit form of $f(x)$:

$$f(x) = f_s \frac{\eta(x)}{n_{\infty\ *}} \exp(cx - \frac{\Gamma g(x)}{\Omega_*}) \quad ,$$

3) the explicit forms of the subintegral functions in the integrals for g and η.

The boundary of this region will be marked by "$-a$". Then the substitution of the low limit of integration by $-a$ is unessential.

Consider L as the functional of two arguments

$$L(y) = L(y, \psi) = \frac{f_s \eta(-\infty)}{n_{\infty\ *}} \exp(cx - \frac{\Gamma y}{\Omega_*}) \exp(-\psi), \tag{2.1.52}$$

$$\psi = f_s \int_{-a}^{z} \exp(cx - \frac{\Gamma y}{\Omega_*}) dx \quad .$$

Then

$$L(y_1) - L(y_2) \leq \max_{-a \leq x \leq b} | \frac{\partial L}{\partial y} | (y_1 - y_2) + \max_{-a \leq x \leq b} | \frac{\partial L}{\partial \psi} | (\psi_1 - \psi_2) \quad . \tag{2.1.53}$$

Introducing

$$||y|| = \max_{-a\leq x\leq z} y \quad , \tag{2.1.54}$$

one can get the following equations

$$L(y_1) - L(y_2) \leq l_1 + l_2 \quad , \tag{2.1.55}$$

where

$$l_1 = \max_{-a\leq x\leq b} | \frac{\partial L}{\partial y} | \, ||y_1 - y_2|| \quad , \tag{2.1.56}$$

$$l_2 = \max_{-a\leq x\leq b} | \frac{\partial L}{\partial \psi} | \, ||y_1 - y_2|| \max_{-a\leq x\leq b} | \frac{d \, \exp(cx - \frac{\Gamma g}{\Omega_*})}{d \, g} | \, (b+a) f_s \quad . \tag{2.1.57}$$

This inequality can be rewritten as

$$L(y_1) - L(y_2) \leq \max_{-a\leq x\leq b} | \frac{\partial L}{\partial y} | \, \omega \quad , \tag{2.1.58}$$

where

$$\omega = [1 + (b+a) \max_{-a\leq x\leq b} | \frac{\partial L}{\partial \psi} | \frac{\exp(\psi) n_\infty}{\eta(-\infty)}] ||y_1 - y_2|| \quad . \tag{2.1.59}$$

Then the last estimate will be the following one

$$L(y_1) - L(y_2) \leq \tilde{\beta} ||y_1 - y_2|| \quad , \tag{2.1.60}$$

where $\tilde{\beta}$ is some constant.

Then

$$g_{b\ (i+1)} - g_{b\ (i)} = \int_{-a}^{z} dx (z-x)^{1/\alpha} [L(g_{b\ (i)}) - L(g_{b\ (i-1)})] \quad , \tag{2.1.61}$$

$$g_{b\ (i+1)} - g_{b\ (i)} \leq \int_{-a}^{z} dx (z-x)^{1/\alpha} ||g_{b\ (i)} - g_{b\ (i-1)}|| \tilde{\beta} \quad , \tag{2.1.62}$$

$$||g_{b\ (i+1)} - g_{b\ (i)}|| \leq \int_{-a}^{z} dx (z-x)^{1/\alpha} ||g_{b\ (i)} - g_{b\ (i-1)}|| \tilde{\beta} \quad , \tag{2.1.63}$$

$$g_{b\ (i+1)} - g_{b\ (i)} \leq (z+a)(a+b)^{1/\alpha} \tilde{\beta} ||g_{b\ (i)} - g_{b\ (i-1)}|| \quad , \tag{2.1.64}$$

$$||g_{b\ (i+1)} - g_{b\ (i)}|| \leq (z+a)(a+b)^{1/\alpha} \tilde{\beta} ||g_{b\ (i)} - g_{b\ (i-1)}|| \quad . \tag{2.1.65}$$

The recurrent procedure leads to

$$||g_{b\ (i)} - g_{b\ (i+1)}|| \leq \frac{(z+a)^i}{i!} const \quad . \tag{2.1.66}$$

The summation of the r.h.s. of the last equation gives the function $const\ \exp(z+a)$. Then the sequence of iterations is the fundamental one. So, it converges. The solution is the unique and it exists.

Inequalities (2.1.39), (2.1.40) allow to estimate errors in $g_{a\ (i)}, \eta_{a\ (i)}$. The measure of the precision is the error of the modern experiment. The most representative characteristic is the total number of the droplets. We shall measure the precision of the theory by the error in the total number of the droplets

$$\Delta_i = \frac{|N_i(\infty) - N(\infty)|}{N(\infty)} \quad . \tag{2.1.67}$$

Due to (2.1.51) one can get the estimate for the precision of the disbalanced iterations

$$\Delta_{a\ (2i)} \leq \frac{\mid N_{a\ (2i+1)}(\infty) - N_{a\ (2i)}(\infty) \mid}{N_{a\ (2i)}(\infty)} \quad . \tag{2.1.68}$$

In the free molecular regime the error of the second iterations is less than 0.16. It can be shown by the comparison of (2.1.49) with expression for

$$N_{a\ (3)} = \eta(-\infty)[1 - \exp(-\frac{Y}{h})] \quad , \tag{2.1.69}$$

where

$$Y = \int_{-\infty}^{\infty} d\xi \exp[\xi - \frac{1}{\gamma(1/\alpha)} \int_{-\infty}^{\xi} (\xi - \sigma)^{1/\alpha} \exp[\sigma - \frac{h+1}{h} \exp(\sigma)] d\sigma] \quad . \tag{2.1.70}$$

The analytical expression for $g_{a\ (2)}$ can not be constructed as well as the further iterations. One can see the problem to construct some more precise approximation for the solution.

One can use the second iteration approximation to justify (2.1.22). If one requires that the relative number before PIFD and after this period would be equal to $\delta/2$ then

$$\frac{\delta}{2} N(\infty) = N(-\Delta_- x) \quad , \quad (1 - \frac{\delta}{2}) N(\infty) = N(\Delta_+ x) \quad . \tag{2.1.71}$$

and for the halfwidths of the spectrum $\Delta_\pm x$ the following expressions

$$\Delta_- x = -\frac{1}{c} \ln(-\frac{c}{h f_s} \ln(1 + \ln(1 - \delta[1 - \exp(-\frac{1}{h}(1 - \exp(-\frac{h f_s}{c})))]))) \quad ,$$

$$\Delta_+ x = \frac{1}{c}\ln(-\frac{c}{f_s h}\ln(1+h\ln(1-(1-\frac{\delta}{2})(1-\exp(-\frac{1}{h})))))$$

can be obtained.

So, the value of $\Delta_\pm x$ has the order of c^{-1}. Then the value of $\Delta\Omega$ has the order of Ω_*/Γ and the first inequality (2.1.22) is justified. The second inequality follows from the first one and from (2.1.24). The variations of ζ, Ω and φ during this period are very small.

The inequalities (2.1.7) and (2.1.14) can be rewritten as

$$c^{-1} \gg \rho_c \quad , \tag{2.1.72}$$

$$t_s \ll \frac{c^{-1}}{\varphi} \quad . \tag{2.1.73}$$

2.1.5 Momentums of the distribution function

In frames of the adopted method of disbalanced iterations it would be interesting to get the expression for $g_{a\ 2}(z)$ but it is impossible to do it analytically. For the free molecular regime $\alpha = 1/3$ and one can get after PIFD the following representation for $g(z)$

$$g(z) = \sum_{i=0}^{3} z^{3-i}\frac{3!(-1)^i}{i!(3-i)!}\hat{g}_i \quad , \tag{2.1.74}$$

where

$$\hat{g}_i = \int_{-\infty}^{\infty} x^i f(x)dx \quad . \tag{2.1.75}$$

For the values $\hat{g}_{a\ i}$ the following chains are valid

$$(\hat{g}_{a\ i})_1 > \hat{g}_{a\ i}\ ,\ (\hat{g}_{a\ i})_2 < \hat{g}_{a\ i}\ ,\ ..., \tag{2.1.76}$$

$$(\hat{g}_{a\ i})_3 < (\hat{g}_{a\ i})_1\ ,\ (\hat{g}_{a\ i})_4 > (\hat{g}_{a\ i})_2\ ,\ .... \tag{2.1.77}$$

This leads to the inequality

$$|(\hat{g}_{a\ i})_{j+1} - (\hat{g}_{a\ i})_j| > |\hat{g}_{a\ i} - (\hat{g}_{a\ i})_j| \quad , \tag{2.1.78}$$

which allows to estimate the precision of the approximation.

In the last equations the external index marks the number of the iterations and the value $(\hat{g}_{a1})_j$ is defined as

$$(\hat{g}_{a\ i})_{j+1} = \frac{f_s}{n_{\infty\ *}}\int_{-\infty}^{\infty} x^i \eta_{a\ j}\exp(cx - \Gamma\frac{g_{a\ j}(x)}{\Omega_*})dx \quad . \tag{2.1.79}$$

The calculation $\hat{g}_{a\ i}$ in the second approximation leads to

$$(\hat{g}_{a\ 1})_2 = \frac{\eta(-\infty)f_s}{n_{\infty\ *}c^2\tilde{\alpha}}[\Psi(1) - \ln\tilde{\alpha}] \quad , \tag{2.1.80}$$

$$(\hat{g}_{a\ 2})_2 = \frac{\eta(-\infty)f_s}{n_{\infty\ *}c^3\tilde{\alpha}}\{[\Psi(1) - \ln\tilde{\alpha}]^2 + \Psi'(1)\} \quad , \tag{2.1.81}$$

$$(\hat{g}_{a\ 3})_2 = \frac{\eta(-\infty)f_s}{n_{\infty\ *}c^4\tilde{\alpha}}\{[\Psi(1) - \ln\tilde{\alpha}]^3 + 3[\Psi(1) - \ln\tilde{\alpha}]\Psi'(1) + \Psi''(1)\} \quad , \tag{2.1.82}$$

where

$$\tilde{\alpha} = \frac{h+1}{c}f_s \quad , \tag{2.1.83}$$

$\Psi(1)$, $\Psi'(1)$, $\Psi''(1)$ are the "psi-function" and the derivatives taken when the argument is equal to 1. The whole dependence on the external parameters is accumulated in the elementary functions.

One can estimate the errors of the obtained expressions and they are really small.

2.1.6 Universal solution

The main idea will be the idea of the squeezed description. Extract the characteristics of the spectrum $f(x)$ which are essential for the condensation process.

The balance equation can be presented in the form (2.1.16). Then the expression for g is described by the values

$$\mu_i = \int_{-\infty}^{z} x^i f(x)dx \quad . \tag{2.1.84}$$

The following expression for g due to the rapid vanishing of $f(x)$ is valid

$$g = \frac{n_{\infty\ *}V_*}{n_\infty V}\int_{-\infty}^{\infty} f(x)(z-x)^{1/\alpha}dx \quad . \tag{2.1.85}$$

Now the evolution is described by the full momentums of the spectrum. The leading term will be

$$g(z) \approx \mu_0(z=\infty)z^{1/\alpha}\frac{n_{\infty\ *}V_*}{n_\infty V} \quad . \tag{2.1.86}$$

This fact will be valid for the arbitrary regime of the droplets growth.

Analyze the convergence of the iterations $g_{a\ (i)}, \eta_{a\ (i)}$. The calculations of (2.1.49), (2.1.69), (2.1.70) show that the error increases when h increases. Then the situation $h \ll 1$ is well described. But the situation $h \gg 1$ is described with the essential error. Also one has to mention that the final approximation in the disbalanced iterations can be obtained without the account of the exhausting of the heterogeneous centers.

When $\eta \equiv \eta(-\infty)$ the balance equation for the heterogeneous centers disappears and the balance equation for the substance resembles the form of the homogeneous condensation. This form can be gotten by the analytical expansion of the solution from the situation where t_* is the moment of the maximum of the supersaturation. One can introduce the function

$$\phi = \Gamma \frac{\Omega_* - \zeta}{\Omega_*} \tag{2.1.87}$$

and get the following universal equation

$$\phi(z) + \frac{1}{\alpha} z \int_{-\infty}^{0} (0-x)^{-1+1/\alpha} \exp(-\phi(x)) dx = \int_{-\infty}^{z} (z-x)^{1/\alpha} \exp(-\phi(x)) dx \tag{2.1.88}$$

in the variables normalized in the appropriate manner[6]. It follows from the previous expression that $\phi(x)$ is the universal function.

The transition from x, z to cx, cz, from the function g to $G = \Gamma g/\Omega_*$ and from the function η to $\Theta = \eta/\eta(-\infty)$ gives the following equations

$$G = A \int_{-\infty}^{z} (z-x)^{1/\alpha} \Theta(x) \exp(x-G) dx \quad , \tag{2.1.89}$$

$$\Theta = \exp[-B \int_{-\infty}^{z} \exp(x-G) dx] \quad , \tag{2.1.90}$$

where the constants A and B are defined by

$$A = \frac{\Gamma f_s \eta(-\infty)}{c^{1+1/\alpha} \Omega_* n_{\infty *}} \quad , \qquad B = \frac{f_s}{c} \quad . \tag{2.1.91}$$

The choice of the basic point in the construction of the approximations (the linearization of the external supersaturation as the function

[6]It will be discussed at the end of this chapter.

of x and the linearization of the free energy as the function of the supersaturation) is essential only when $h \gg 1$. In the opposite situation $h \ll 1$ the result is evident. All heterogeneous centers are the centers of the droplets. When the parameters of the ideal supersaturation are fixed the relative sizes of the region $\Delta_g\Omega$ of the values Ω_*, corresponding to all situations except $h \ll 1$, are rather small

$$\frac{\Delta_g\Omega}{\Omega_*} \leq \frac{\epsilon}{\Gamma} \qquad \epsilon \sim 3 \tag{2.1.92}$$

The inequalities mentioned above are so strong that the linearization is valid in the more large region than $\Delta_g\Omega$. Then the choice of the point in this interval as the basic point of the approximation leads to the applicability of the linearization in all situations except $h \ll 1$. Then one can use as the basic point of the mentioned approximations the moment when the half of the total droplets is formed in the pseudo homogeneous situation. Then for $A = A_0 = \frac{1}{\alpha}\int_{-\infty}^{0}(0-x)^{-1+1/\alpha}\exp(-\phi(x))dx$ one can have the fixed value. For example, $A_0 = 0.136$ in the case $\alpha = 1/3$.

As far as the influence on the evolution occurs due to $\{\mu_i\}$ and $\int_{-\infty}^{z}\exp(x - G(x))dx$ only one rather arbitrary numerical calculation is necessary. One isn't interested in the precise determination of t_* but only in the determination $\mu_0(x = \infty)$ (and $\int_{-\infty}^{0}(0-x)^{-1+1/\alpha}f(x)dx$). Instead of $(1/\alpha)\int_{-\infty}^{0}(0-x)^{-1+1/\alpha}\exp(-\phi(x)dx$ we can take some constant ($\sim 1/5$ in the case $\alpha = 1/3$). The result of the calculations gives the total number of the droplets.

Suppose that the solution has the maximum at z_0. Then it gives the algebraic equation on the parameters of the process.

The concrete A_0 allows to justify (2.1.72), (2.1.73) for all situations except $h \ll 1$. Taking for t_s the Zeldowitch estimate where $W^+_{\nu_c}$ is the coefficient of absorption which can be estimated as

$$\frac{W^+_{\nu_c}}{\nu_a^{1-\alpha}} \sim \varphi$$

one can justify the mentioned inequality. The height of the activation barrier ΔF can be estimated by the homogeneous value $F\mid_{\nu=\nu_c}$. According to the Gibbs equation this value is proportional to the surface square

$$F_c \sim \rho_c^{\frac{1}{\alpha}\frac{dim-1}{dim}} \tag{2.1.93}$$

(dim is the dimension of the space). Then we can justify the required

inequalities[7].

In the application to the iteration procedure the first and the second approximation for η will coincide as far as $g_{a\ (0)} = g_{a\ (1)} = g_\infty$. It is impossible to get the analytical expression in the second approximation for g and in the third approximation for η. Then consider the reduced iterations[8]. The first iteration takes into account the exhausting of the heterogeneous centers

$$G_{(1)} = A_0 \int_{-\infty}^{z} dx (z-x)^{1/\alpha} \exp(-B \int_{-\infty}^{x} d\xi \exp(\xi - G_\infty(\xi))) \exp(x - G_\infty(x)) \quad , \tag{2.1.94}$$

where G_∞ is the pseudo homogeneous solution.

The relative number of the heterogeneous centers occupied by the droplets can be obtained on the base of

$$N^+_{(2)}(\infty) \sim \int_{-\infty}^{\infty} f(x)dx \sim \int_{-\infty}^{\infty} \exp(x - G_{(1)})dx \quad . \tag{2.1.95}$$

As far as

$$N^+_{(1)}(z) \sim \int_{-\infty}^{z} d\xi \exp(\xi - G_\infty) \tag{2.1.96}$$

is the universal function one can construct the universal expansion on the first step. After the decomposition of the exponent one can get

$$N^+_{(2)}(\infty) \sim \int_{-\infty}^{\infty} dz \exp(z - A_0 Q_0(z)) \prod_{l=1}^{\infty} D_l \quad , \tag{2.1.97}$$

where

$$D_j = \sum_{l=0}^{\infty} (\frac{(-1)^j B^j}{j!} Q_j A_0)^l \frac{1}{l!} \quad , \tag{2.1.98}$$

$$Q_i = \int_{-\infty}^{z} dx (z-x)^{1/\alpha} \exp(x - G_\infty(x)) N^i_{(1)}(x) \tag{2.1.99}$$

[7] See one of the next sections

[8] At the first iterations they will coincide with the disbalanced ones with the shifted number of the approximation.

This leads to the following representation

$$N^{+}_{(2)}(\infty) \sim \sum_i P_i B^i \quad , \tag{2.1.100}$$

where P_i are some constants. This expression can be linearized as function of B as far the result will be substituted into the exponential form for the number of the free heterogeneous centers and the very high accuracy isn't necessary. Then

$$N^{+}_{(2)}(\infty) = P_0 + P_1 B \quad , \tag{2.1.101}$$

where

$$P_0 = \int_{-\infty}^{\infty} \exp[x - A_0 Q_0] dx \quad , \tag{2.1.102}$$

$$P_1 = \int_{-\infty}^{\infty} \exp[x - A_0 Q_0] Q_1 dx A_0 \quad . \tag{2.1.103}$$

Then the final expressions will be the following

$$N^{+}(\infty) = 1 - \exp[-B(P_0 + P_1 B)] \quad . \tag{2.1.104}$$

In the case $\alpha = 1/3$ the characteristic value of the error has the order of one percent.

The expressions for the other momentums can be obtained analogously.

* * *

The nonisothermal effects can be included into the given picture. The renormalizations for the rate of nucleation and the rate of growth are known and they are quasi integrals during PIFD.

Also two mentioned assumptions can be proved.

The intensity of the heat extracting doesn't depend on the size of the embryo. According to the Klapeiron-Klausius equation this leads to the fixed increase of the temperature and of the supersaturation.

The central moment is the smallness of the deviation of the supersaturation from the external supersaturation[9] of the order Γ^{-1}. The vapor consumption and the heat extraction lead to the same effect - to the decrease of the supersaturation. Then the relative deviation of the temperature is very small and one can linearize the exponent in

[9] Γ has to be renormalized but remains the big constant parameter.

the Klipeiron-Klausius equation. Then the nonisothermal effects can be taken into account by the simple renormalization. By the sequential increasing of the nonisothermal effects from the situation of their absence one can show the possibility to linearize the exponent[10]. All necessary inequalities can be justified.

Here the temperature is the ordinary thermodynamic parameter. As far as the Klapeiron-Klausius equation was linearized the form of this equation isn't too important. These conclusions can be made for the inclusion of the arbitrary thermodynamic parameter. æ

2.2 The distribution of the droplets in the process of condensation

Instead of the exponential approximation one can use the power approximation. It allows to take into account the discreet character of the number of the molecules in the embryo.

2.2.1 Approximation of the nucleation rate

In the homogeneous case one can get the following inequality for $\zeta_1 > \zeta_2$:

$$\frac{f_{s\ hom}(\zeta_1)}{f_{s\ hom}(\zeta_2)} > \exp(F_c(\zeta_2) - F_c(\zeta_1)) \quad . \tag{2.2.1}$$

One can show that during PIFD

$$F_c(\zeta_*) - F_c(\zeta) \leq 1 \quad , \tag{2.2.2}$$

where ζ_* is the maximum of the supersaturation. In this region the following estimate is valid

$$\frac{f_{s\ hom}(\zeta_1)}{f_{s\ hom}(\zeta_2)} \approx \exp(F_c(\zeta_2) - F_c(\zeta_1)) \tag{2.2.3}$$

The next step is the approximation of $F_c(\zeta_2) - F_c(\zeta_1)$. Decomposition of this function as the function of $\ln(\zeta)$ gives

$$F_c(\zeta_2) - F_c(\zeta_1) \approx \nu_c \ln(\frac{\zeta_2}{\zeta_1}) \quad . \tag{2.2.4}$$

[10]The parameters of the process will change many times. But the form of the spectrum will be the same.

The error has the order

$$\delta_1 = \frac{3}{2\ln(\zeta_1)}\nu_c^{-1} = \frac{9}{4a}\rho_c^{-2} \quad , \tag{2.2.5}$$

which is negligible. The linearization on ζ gives

$$\Delta F(\zeta_2) - \Delta F(\zeta_1) \approx \nu_c \ln(\frac{\zeta_2}{\zeta_1}) \approx \nu_c \frac{\zeta_2 - \zeta_1}{\zeta_1} \tag{2.2.6}$$

with the error of the order

$$\delta_2 = \frac{9}{4a}\rho_c^{-2} + \frac{1}{2}\rho_c^{-3} \quad , \tag{2.2.7}$$

which has rather more complicate structure.

It will be important that $\frac{dF_c}{d\ln(\zeta)} = \nu_c$ is supposed to be integer[11]. Really, the number of the molecules is integer.

In the heterogeneous case this approximation has to be checked directly. When the supersaturation is very small this approximation will be valid as far as the main influence occurs due to the pseudo homogeneous behavior of the free energy of the near critical embryo.

Instead of (2.2.3) one can get

$$\frac{f_{s\ het}(\zeta_1)}{f_{s\ het}(\zeta_2)} \approx \exp(\Delta F(\zeta_2) - \Delta F(\zeta_1)) \quad . \tag{2.2.8}$$

The linearization on $\ln(\zeta)$ gives the following expression

$$F(\zeta_2) - F(\zeta_1) \approx \frac{d\Delta F}{d\ln(\zeta)} \ln(\frac{\zeta_2}{\zeta_1}) \quad . \tag{2.2.9}$$

It is important that $\frac{d\Delta F}{d\ln(\zeta)}$ is integer.

Really, the thermodynamic expression for the free energy as the decomposition on the inverse radius has the following form

$$F_{het} = -\ln(\zeta)\nu + a\nu^{2/3} + c_{-1}\nu^{1/3} + c_0\ln(\nu) + \sum_{i=1}^{n} c_i\nu^{-i/3} + const \quad . \tag{2.2.10}$$

[11] As far as the zero of the derivatives of the surface tension on the size is attained at noninteger number of the molecules inside the embryo there is some error is these considerations.

The coefficients c_i depend on ζ rather weakly as far as they are connected with the structure of the rather solid nuclei. We shall neglect this dependence.

The value $\frac{d\Delta F}{d\ln(\zeta)}$ can be expressed in the following manner

$$\frac{d\Delta F}{d\ln(\zeta)} = \frac{dF_{het}(\nu_c)}{d\ln(\zeta)} - \frac{dF_{het}(\nu_e)}{d\ln(\zeta)} \quad . \tag{2.2.11}$$

For $\frac{dF_{het}(\nu)}{d\ln(\zeta)}$ and $\frac{dF_{het}(\nu_e)}{d\ln(\zeta)}$

$$\frac{dF_{het}(\nu_e)}{d\ln(\zeta)} = \frac{\partial F_{het}(\nu)}{\partial\ln(\zeta)} + \frac{\partial F_{het}(\nu)}{\partial\nu}\frac{\partial\nu}{\partial\ln(\zeta)} \quad . \tag{2.2.12}$$

When $\nu = \nu_c$ or $\nu = \nu_e$, the second term goes to zero. According to (2.2.10) one can calculate the first term in the last equation by the differentiating of the leading term in the asymptotic expansion. As the result one can have for $\nu = \nu_c$ or $\nu = \nu_e$

$$\frac{dF_{het}(\nu)}{d\ln(\zeta)} = -\nu \quad . \tag{2.2.13}$$

Then for the height of the activation barrier one can get

$$\frac{d\Delta F}{d\ln(\zeta)} = \nu_c - \nu_e \quad . \tag{2.2.14}$$

As far as ν_c and ν_e are integer the result in the r.h.s. is integer also. Finally

$$\frac{f_{s\ het}(\zeta_1)}{f_{s\ het}(\zeta_2)} \approx (\frac{\zeta_1}{\zeta_2})^{\nu_c-\nu_e} \quad . \tag{2.2.15}$$

The linearization of F_{het} on ζ leads to the additional error of the following form

$$\frac{f_{s\ het}(\zeta_1)}{f_{s\ het}(\zeta_2)} \approx \exp((\nu_c - \nu_e)\frac{\zeta_1 - \zeta_2}{\zeta_2}) \quad . \tag{2.2.16}$$

The next task is the construction of the spectrum

$$f^+(x) = f_{s\ hom}(\zeta(x)) \tag{2.2.17}$$

in the homogeneous case and

$$f^+(x) = f_{s\ het}(\zeta(x))\eta \tag{2.2.18}$$

in the heterogeneous case.

2.2.2 Homogeneous decay

The basic value of the supersaturation ζ_0 will be the initial supersaturation in the system.

The balance equation will be the following[12]

$$\zeta(z) = \zeta_0 - \frac{f_{s\ hom}(\zeta_0)}{n_{\infty\ *}} \int_0^z (z-x)^3 (\frac{\zeta(x)}{\zeta_0})^{\nu_c(\zeta_0)} dx \quad . \tag{2.2.19}$$

The iteration procedure is constructed as the following one

$$\zeta_i = D(\zeta_{i-1}) \quad , \tag{2.2.20}$$

where

$$D(v) = \zeta_0 - \frac{f_{s\ hom}(\zeta_0)}{n_{\infty\ *}} \int_0^z (z-x)^3 (\frac{v(x)}{\zeta_0})^{\nu_c(\zeta_0)} dx \quad . \tag{2.2.21}$$

The initial approximation is

$$\zeta_1 = \zeta_0 \quad . \tag{2.2.22}$$

Operator D has the following property for the positive v_1 and v_2. When

$$v_1 > v_2 \tag{2.2.23}$$

for all x, then

$$D(v_1) < D(v_2) \tag{2.2.24}$$

for all x. For the arbitrary $v > 0$

$$D(v) < \zeta_0 \quad . \tag{2.2.25}$$

Note that

$$\zeta_1 > \zeta \tag{2.2.26}$$

for all x where ζ is the precise solution of (2.2.19). Then one can get

$$\zeta_i < \zeta \tag{2.2.27}$$

for all even i and

$$\zeta_i > \zeta \tag{2.2.28}$$

for all odd i.

[12] In the free molecular regime after the standard transformations. The value of $f_{s\ hom}(\zeta_0)$ is the amplitude of the spectrum (not in the units of n_∞).

According to (2.2.25)

$$\zeta_3 < \zeta_1 \tag{2.2.29}$$

for all x and one can get the following chain

$$\begin{aligned} \zeta_2(x) < \zeta_4(x) < ... < \zeta_{2i}(x) < ... < \zeta_(x) < ... \\ < \zeta_{2i+1}(x) < ...\zeta_3(x) < \zeta_1(x) \quad . \end{aligned} \tag{2.2.30}$$

The last chain gives the estimate for the precision of the iterations. The uniqueness of the solution follows from the reduction of (2.2.19) to the ordinary differential equation of the forth order with the initial condition at t_*.

If v is the polynomial of the order t, then $D(v)$ is also the polynomial with the order less than $\nu_c t + 4$. So one can calculate here all iterations.

The velocity of the convergence is rather high and the error of the third iteration in the supersaturation is less than 0.02 at the upper boundary of PIFD.

2.2.3 Homogeneous condensation in the dynamic conditions

In the dynamic external conditions in frames of the standard transformations after the account of (2.2.4) one can get

$$\zeta(z) = \Phi(z) - \frac{f_{s\ hom}(\zeta_0)}{n_{\infty\ *}} \int_{-\infty}^{z} (z-x)^3 (\frac{\zeta(x)}{\zeta_0})^{\nu_c(\zeta_0)} dx \quad . \tag{2.2.31}$$

One needn't the linearization of $\Phi(z)$. We can use the more wide class of the functional dependencies[13]

$$\Phi(z) = \sum_j \Theta(z - z_j) \sum_i c_{ij} z^i + \Phi_* \quad . \tag{2.2.32}$$

All results of the previous section will be valid[14] after the substitution

$$D(v) \to R(v) = \Phi_* + \sum_j \Theta(z - z_j) \sum_i c_{ij} z^i$$

[13]Here and later we write Φ instead Ω. The basic point ζ_0 is necessary to put equal to Φ_*.

[14]Here the value $f_{s\ hom}(\zeta_0)$ has the same functional dependence as in the previous case.

(2.2.33)

$$-\frac{f_{s\ hom}(\zeta_0)}{n_{\infty\ *}}\int_{-\infty}^{z}(z-x)^3(\frac{\zeta(x)}{\zeta_0})^{\nu_c(\zeta_0)}dx \quad ,$$

$$\zeta_1 \to \sum_j \Theta(z-z_j)\sum_i c_{ij}z^i + \Phi_* \quad . \tag{2.2.34}$$

All iterations can be calculated in the polynomial form.

For the dependencies of $\Phi(z)$ with the negative second derivatives z the function ζ_3 has the error during PIFD less than 0.05.

All iterations can be calculated analytically.

2.2.4 Heterogeneous condensation

The system of the heterogeneous condensation with the help of (2.2.9) can be reduced to the following equations

$$\zeta(z) = \psi - \frac{f_{s\ het}(\zeta(z=0))}{n_{\infty\ *}}$$

(2.2.35)

$$\int_b^z (z-x)^3(\frac{\zeta(x)}{\zeta(z=0)})^{(\nu_c(\zeta(z=0))-\nu_e(\zeta(z=0)))}\eta(x)dx \quad ,$$

$$\eta(z) = \eta_{tot}\exp(-f_{s\ het}(\zeta(z=0))$$

(2.2.36)

$$\int_b^z (\frac{\zeta(x)}{\zeta(z=0)})^{(\nu_c(\zeta(z=0))-\nu_e(\zeta(z=0)))}dx) \quad ,$$

where $\psi = \zeta_0$, $b = 0$ in the case of the decay and $\psi = \Phi(z)$, $b = -\infty$ in the case of the dynamic conditions[15].

The iterations are now defined as

$$\zeta_{i+1} = P(\zeta_i, \eta_i) \quad , \tag{2.2.37}$$

$$\eta_{i+1} = Q(\zeta_i) \quad , \tag{2.2.38}$$

where

$$P(v,w) = \psi - \frac{f_{s\ het}(\zeta(z=0))}{n_{\infty\ *}}$$

(2.2.39)

$$\int_b^z (z-x)^3(\frac{v(x)}{\zeta(z=0)})^{(\nu_c(\zeta(z=0))-\nu_e(\zeta(z=0)))}w(x)dx \quad ,$$

[15]Here the value $f_{s\ het}$ has the same sence but for the heterogeneous process.

$$Q(v) = \tag{2.2.40}$$
$$\eta_{tot} \exp(-f_{s\ het}(\zeta(z=0)) \int_b^z (\frac{v(x)}{\zeta(z=0)})^{(\nu_c(\zeta(z=0))-\nu_e(\zeta(z=0)))} dx) \quad .$$

One can prove analytically the following properties of P and of Q for the positive values of v_1, v_2, w_1, w_2, v, w:

- When for all x
$$v_1 > v_2 \quad , \qquad w_1 > w_2 \quad , \tag{2.2.41}$$
then
$$P(v_1, w_1) < P(v_2, w_2) \quad . \tag{2.2.42}$$

- When for all x
$$v_1 > v_2 \quad , \tag{2.2.43}$$
then
$$Q(v_1) < Q(v_2) \quad . \tag{2.2.44}$$

- For the arbitrary v, w
$$P(v, w) < \psi \quad . \tag{2.2.45}$$

- For the arbitrary v
$$Q(v) < \eta_{tot} \quad . \tag{2.2.46}$$

The initial approximation is

$$\zeta_1 = \psi \quad , \qquad \eta_1 = \eta_{tot} \quad . \tag{2.2.47}$$

This leads to

$$\zeta_2(x) < \zeta_4(x) < ... < \zeta_{2i}(x) < ... < \zeta_(x) < ... \tag{2.2.48}$$
$$< \zeta_{2i+1}(x) < ...\zeta_3(x) < \zeta_1(x) \quad ,$$

$$\eta_2(x) < \eta_4(x) < ... < \eta_{2i}(x) < ... < \eta(x) \tag{2.2.49}$$
$$< ... < \eta_{2i+1}(x) < ... < \eta_3(x) < \eta_1(x) \quad .$$

The exponential form of Q destroys the polynomial form of the approximations. Note that (2.2.36) is the resolved form of the differential equation.

$$\frac{d\eta(z)}{dz} = -f_{s\ het}(\zeta(z=0))(\frac{\zeta(x)}{\zeta(z=0)})^{(\nu_c(\zeta(z=0))-\nu_e(\zeta(z=0)))}\eta(x) \quad . \tag{2.2.50}$$

We can solve this equation with the given ζ by the iterations

$$\eta_{i\ j+1} = S(\eta_{i\ j}, \zeta_i) = S^j(\eta_{tot\ i}, \zeta_i) \quad , \tag{2.2.51}$$

where

$$S(\eta, \zeta) = -\int_b^z f_{s\ het}(\zeta(z=0))(\frac{\zeta(x)}{\zeta(z=0)})^{(\nu_c(\zeta(z=0))-\nu_e(\zeta(z=0)))}\eta(x)dx \quad .$$

Operator S has the same properties as Q has for η with the given ζ. If we substitute Q in the even iterations by S^{2j+1} and in the odd iterations by S^{2j}, then the structure of (2.2.48), (2.2.49) will be conserved. It is absolutely sufficient[16] to put $j = 1$. Now the polynomial structure of iterations is conserved.

One can use in the iteration procedure initiated by S the value of η calculated on the previous step of the external iteration procedure as the initial approximation and take the proper number of the iterations.

The third iteration guarantees the write form of the spectrum in the situation of the decay. The forth iteration is sufficient in the situation of the dynamic conditions with the negative second derivative of Φ in time.

The processes of the recombinations of the heterogeneous centers and the source of the heterogeneous centers can be included in this scheme by the direct generalization with the possibility of the calculation of the iterations in the polynomial form. æ

[16] We can use as the initial approximation the value of η at the previous step of the iteration procedure with the odd number of the iterations.

2.3 The main characteristics of the nucleation process

2.3.1 The main characteristics of the condensation on the ions. External iterations.

The algebraic equation for the parameters of the condensation (for the free molecular regime) has the following form

$$\frac{f_s}{c} = H(h) \quad , \tag{2.3.1}$$

where $H(h)$ is defined according to

$$H(h) = -\frac{1}{h}\ln(h\ln\frac{\exp(\frac{1}{h})+1}{2}) \quad . \tag{2.3.2}$$

The value of f_s can be presented as

$$f_s = q\exp(-\Delta F(\Phi_*)) \quad , \tag{2.3.3}$$

with the smooth function

$$q = \frac{3\nu_c^{2/3}(\Phi_*+1)}{\sqrt{\pi}\Delta\nu_c\Delta\nu_e\Phi_*} \tag{2.3.4}$$

and the sharp part $\exp(-\Delta F(\Phi_*))$.

For the free energy F_ν of the embryo on the ion with the charge Q the following approximation can be written

$$F_\nu = -\ln(1+\zeta)\nu + a\nu^{2/3} - \lambda a\nu^{1/3} + \frac{1}{2}a\nu_0\nu^{-1/3} \quad , \tag{2.3.5}$$

where

$$\nu_0 = \frac{(1-\epsilon^{-1})Q^2}{3v_l\Gamma} \quad . \tag{2.3.6}$$

Here ϵ is the dielectric constant and λ is associated with the microscopic corrections.

The values of ν_e, ν_c are the roots of equation

$$-2\nu^{4/3}\ln(1+\zeta) + \frac{4}{3}a\nu - \frac{2}{3}\lambda a\nu^{2/3} - \frac{1}{3}a\nu_0 = 0 \quad . \tag{2.3.7}$$

Then for ΔF one can get

$$\Delta F = -\ln(1+\zeta)(\nu_c - \nu_e) + a(\nu_c^{2/3} - \nu_e^{2/3}) \\ -\lambda a(\nu_c^{1/3} - \nu_e^{1/3}) + \frac{a\nu_0}{2}(\nu_c^{-1/3} - \nu_e^{-1/3}) \quad . \tag{2.3.8}$$

The value $\Delta\nu_c$ can be found as

$$\Delta\nu_c = 3|-a\nu_c^{-4/3} + \lambda a\nu_c^{-5/3} + a\nu_0\nu_c^{-7/3}|^{-1/2} \quad . \tag{2.3.9}$$

The equation for Φ_* can be solved by iterations

$$\Delta F(\Phi_{*i+1}) = -\ln[\frac{H(h(\Phi_{*i}))c(\Phi_{*i})}{q(\Phi_{*i})}] \quad . \tag{2.3.10}$$

According to the definitions of c, q one can get

$$\frac{c}{q} = \frac{\sqrt{\pi}\Delta\nu_e\Delta\nu_c m\Gamma\tau_*}{3\alpha t_\infty \Phi_*^{1/m}\nu_c^{2/3}(\Phi_*+1)} \quad , \tag{2.3.11}$$

where m, t_∞ are the parameters in the model law

$$\Phi = (\frac{t}{t_\infty})^m \quad .$$

So, the l.h.s. of the last equation decreases monotonously when Φ_* decreases (t_∞, m being fixed). According to the definition of c the value of the parameter h increases monotonously when Φ_* grows (t_∞, m being fixed).

As far as ν_c is greater than ν_e the big error in ν_e leads to the small errors in ΔF, Γ.

The value of $H(h)$ doesn't depend monotonously on h but comes to the asymptotes

$$H(h) = \frac{\ln 2}{h} \quad h \gg 1 \quad , \tag{2.3.12}$$

$$H(h) = \ln 2 \quad h \ll 1 \quad . \tag{2.3.13}$$

The uniqueness of the solution is evident.

Approximate (2.3.1) by

$$\frac{f_s}{c} = H'(h) \quad , \tag{2.3.14}$$

where

$$H'(h) = \ln 2 \ , \quad 0 < h < 1 \ ,$$
$$H'(h) = \frac{\ln 2}{h} \ , \quad h > 1 \ . \tag{2.3.15}$$

The iterations constructed according to

$$\Delta F(\Phi_{*i+1}) = -\ln[\frac{H'(h(\Phi_{*i}))c(\Phi_{*i})}{q(\Phi_{*i})}] \tag{2.3.16}$$

will estimate the solution from below and from above. The big value of Γ leads to the rapid convergence of iterations. The following chains

$$\Phi_{*\ 1} < \Phi_{*\ 3} < ... < \Phi_{*\ 2i+1} < ... < \Phi_* < ... < \Phi_{*\ 2i} < ... < \Phi_{*\ 4} < \Phi_{*\ 2} \ , \tag{2.3.17}$$

or

$$\Phi_{*\ 2} < \Phi_{*\ 4} < ... < \Phi_{*\ 2i} < ... < \Phi_* < ... < \Phi_{*\ 2i+1} < ... < \Phi_{*\ 3} < \Phi_{*\ 1} \ . \tag{2.3.18}$$

will take place. The accuracy can be estimated

$$|\Phi_{*\ i} - \Phi_*| \leq |\Phi_{*\ i} - \Phi_{*\ i+1}| \quad . \tag{2.3.19}$$

One can show that

$$\frac{H'(h)}{2} < H(h) < \frac{3H'(h)}{2} \tag{2.3.20}$$

It leads to the practically precise definition of the root of the initial equation after the substitution in the iteration procedure of the solution of the reduced equation.

2.3.2 Internal iterations

To find the value of the supersaturation on the base of the activation barrier one can use the initial iterations.

The parameter responsible for the rate of convergence of the iterations is the following

$$R = |\frac{dF_{\nu_c}/d\Phi_*}{dF_{\nu_e}/d\Phi_*}| \gg 1 \tag{2.3.21}$$

Near the boundary of the barrier character of the condensation the value of R goes to the unity. In this case one can use some decompositions based on the smallness of the parameter $(\nu_c - \nu_e)/\nu_c$.

The iteration procedure will be the following. The value of the given supersaturation leads to the size of the equilibrium embryo which leads to the value of the free energy of the equilibrium embryo which leads to the value of the free energy of the critical embryo which leads to the value of number of the molecules in the critical embryo and to the new value of the supersaturation.

The following inequality

$$|\frac{\Phi_*^0 - \Phi_*}{\Phi_*^j - \Phi_*}| \leq [\frac{max|dF_{\nu_e}/d\Phi_*|}{min|dF_{\nu_e}/d\Phi_*|}]^j \quad , \tag{2.3.22}$$

is valid. The upper index denotes the number of the internal iterations. The maximal and the minimal values are taken in the interval from the zero approximation to the real solution. This value is close to R^{-j}. If the zero approximation is less than the real solution then the rate is estimated by R^{-j} from below.

The internal iterations have to the coordinated with the external iterations to ensure the previous chain of inequalities.

This method can be also used for the nonisothermal effects.

For the homogeneous condensation one has to put parameter h to

$$h = \frac{6\bar{\Gamma}}{\Phi_* c^3} \quad . \tag{2.3.23}$$

and to use for H the asymptote $\ln 2/h$.

2.3.3 Modified method

Introduce the variables

$$\tilde{\beta} = \frac{2}{a}\nu_0^{1/3}\ln(1+\Phi_*) \ , \quad u = \frac{\nu}{\nu_0} \quad . \tag{2.3.24}$$

Then F_ν can be written as

$$F_\nu = a\nu_0^{2/3}(-\frac{1}{2}\tilde{\beta}u + u^{2/3} + \frac{1}{2}u^{-1/3}) \quad . \tag{2.3.25}$$

When $\tilde{\beta} = 1$ the values $u_e = \nu_e/\nu_0$, $u_c = \nu_c/\nu_0$ are equal to unity and there is no activation barrier. So, we shall consider only the interval $0 < \tilde{\beta} < 0.94$.

Suppose that for $\Delta\nu_e$ the same approximation as for $\Delta\nu_c$ is valid. Then for q one can get

$$q \sim (1 - 1/u_c)^{1/2} u_e^{-2/3} |1 - 1/u_e|^{1/2} \tag{2.3.26}$$

When $\tilde{\beta}$ increases, then u_e increases. It increases from 0.25 to 0.634 in the considered interval of the supersaturation and u_c decreases from ∞ to 1.842. The value $(1 - u_c^{-1})^{1/2} u_e^{-2/3} |1 - u_e^{-1}|^{1/2}$ from the r.h.s. of the last equation decreases monotonically, the relative variation of this value (and of q) is less than 5.3. This value is many times less than the variation of $\exp(-\Delta F(\zeta))$ which allows to consider q

Consider the situation $h \geq 1$. The situation $h \leq 1$ can be considered analogously and the error of ΔF there is smaller there. Rewrite the equation with the explicit expressions for f_s and c

$$\Delta F(\Phi_*) = \ln q + \ln(\frac{\eta_{tot}}{n_{\infty *}}) + \\ 4 \ln \alpha + \ln 6 - 3 \ln \Gamma - 4 \ln \tau A + 7 \ln \Phi_* - \ln \ln 2 \ , \tag{2.3.27}$$

where $A = d\Phi/dt$.

In the zero approximation one can neglect $\ln \Gamma$ and $\ln \Phi_*$ in the last equation. In the heterogeneous case the value of Γ isn't so great as in the homogeneous case.

When $h \gg 1$ one can put for the estimates $N(\infty) \sim A^3$, $f_s \sim A^4$. So, $N(\infty)$ grows when Φ_* grows. When Φ_* grows the barrier character can be violated. So, the intensive nucleation occurs near the upper boundary of the region under the consideration. When $\ln \Gamma$ and $\ln \Phi_*$ are neglected in the r.h.s. of the last equation then the error in the height of the activation barrier is $\ln \Gamma$. Then for Γ and Φ_* in the r.h.s. of the last equation one can take $\Gamma(\Phi_b)$ and Φ_b, where $\Phi_b = \exp(a\tilde{\beta}/2\nu_0^{1/3})|_{\tilde{\beta}=0.94} - 1$ is obtained with the relative error $3|\ln \Gamma(\Phi_b)/\Gamma(\Phi_b)|$. When Φ_* is near Φ_b then there is practically no error in the determination of the r.h.s., when Φ_* is far from Φ_b then the force of the iterations is great. So, for $\Delta F(\Phi_*)$ the following expression is valid

$$\Delta F(\Phi_*) = \ln(q|_{\tilde{\beta}=0.8}) + \ln \frac{\eta(-\infty)}{n_{\infty *}} \\ +7 \ln \Phi_b - 3 \ln \Gamma(\Phi_b) - 4 \ln(\frac{A\tau}{\alpha}) \ . \tag{2.3.28}$$

The problem is reduced to find Φ_* on ΔF. Divide the interval $0 < \tilde{\beta} < 0.94$ into two parts $0 < \tilde{\beta} < 0.68$ and $0.68 < \tilde{\beta} < 0.94$. Note that $dF_{\nu_e}/d\tilde{\beta} = -u_e a\nu_0^{2/3}/2$ and $dF_{\nu_c}/d\tilde{\beta} = -u_c a\nu_0^{2/3}/2$. When $\tilde{\beta} < 0.68$, $u_c \gg u_e$ the following way is effective: $\tilde{\beta}$ is found on the value of $F_{\nu_c}(\tilde{\beta})$, which is equal to $F_{\nu_e}|_{\tilde{\beta}=0} + \Delta F$. The relative precision of the determination of $\tilde{\beta}$ can be estimated as

$$\frac{\Delta\tilde{\beta}}{\tilde{\beta}} \leq |\frac{u_e|_{\tilde{\beta}=0.68}}{u_c|_{\tilde{\beta}=0.68}}| \quad .$$

So, the error of the determination of $\tilde{\beta}$ is rather small. In the considered interval of $\tilde{\beta}$ the value u_e is near $u_e|_{\tilde{\beta}=0} = 1/4$ which allows to improve the accuracy. Consider ΔF as the difference between $\hat{F}_{\nu_c} = F_{\nu_c} + \frac{1}{2}u_e|_{\tilde{\beta}=0}\tilde{\beta}a\nu_0^{2/3}$ and $\hat{F}_{\nu_e} = F_{\nu_e} + \frac{1}{2}u_e|_{\tilde{\beta}=0}\tilde{\beta}a\nu_0^{2/3}$ and find $\tilde{\beta}$ on the base of the value of $\hat{F}_{\nu_c}(\tilde{\beta})$, which is equal to $\Delta F + \hat{F}_{\nu_e}|_{\tilde{\beta}=0} = \Delta F + F_{\nu_e}|_{\tilde{\beta}=0}$. The relative error of β can be estimated as

$$\frac{\Delta\tilde{\beta}}{\tilde{\beta}} \leq |\frac{u_e|_{\tilde{\beta}=0.68} - u_e|_{\tilde{\beta}=0}}{u_c|_{\tilde{\beta}=0.68} - u_e|_{\tilde{\beta}=0}}| \quad .$$

The calculation shows that the accuracy $\Delta\tilde{\beta}/\tilde{\beta}$ is less than 2.5 percents. This procedure can be generalized by taking into account in the transition from F_{ν_e} to $\hat{F}_{\nu_e}$ the terms of the decomposition of F_{ν_e} on $\tilde{\beta}$ and calculating the next approximation according (2.3.26). The value of $\tilde{\beta}$ can be calculated as the root of equation

$$[-\frac{1}{2}(\frac{4}{3}u_c^{-1/3} - \frac{1}{3}u_c^{-4/3})u_c + u_c^{2/3} + \frac{1}{2}u_c^{-1/3} + \frac{1}{8}(\frac{4}{3}u_c^{-1/3} - \frac{1}{3}u_c^{-4/3})] = \frac{\Delta F + F_{\nu_e}|_{\tilde{\beta}=0}}{a\nu_0^{2/3}} \quad . \tag{2.3.29}$$

The neglecting of $u_c^{-4/3}/24$ leads to the small relative errors in the determination of $\tilde{\beta}$ and the last equation is reduced to the cubic equation.

When $0.68 < \tilde{\beta} < 0.94$ on the base of ΔF the value of $\tilde{\beta}$ can be found by the simple interpolation formula

$$\tilde{\beta} = 0.1136(\frac{3\Delta F}{a\nu_0^{2/3}})^2 - 0.3465\frac{3\Delta F}{a\nu_0^{2/3}} + 0.9513 \quad .$$

The relative error of the determination of $\tilde{\beta}$ is less than 2 percents.

The choice of intervals $\tilde{\beta}$ is solved by the direct calculation in (2.3.1) of the value A when $\tilde{\beta} = 0.68$. Analogously one can solve the question about the choice of the asymptotes of H' (it is necessary to find $\tilde{\beta}$ when $h = 1$ with given A, then the new A is calculated).

Determine now Φ_*. On the base of $\tilde{\beta}$ the value of Φ_* can be found as

$$\Phi_* = \exp(\frac{\tilde{\beta}a}{2\nu_0^{1/3}}) - 1 \quad .$$

The function $[\Phi_*/(\Phi_* + 1)] \ln^{-1}(1 + \Phi_*)$ connects the relative errors of $\tilde{\beta}$ and of Φ_*. It is changed mainly due to $\ln(1 + \Phi_*)$. Taking into account that $\Phi_* > 1$, $\ln(1 + \Phi_*) < \frac{0.94a}{2\nu_0^{1/3}}$ one can come to the fact that near Φ_b the relative errors of $\tilde{\beta}$ and Φ_* have one and the same order. Then $\Delta\Phi/\Phi_* \sim [3|\ln(\Gamma/\Gamma(\Phi_b))|/\Gamma + 0.025]$ which ensure the precise definition of Φ_*.

When $\tilde{\beta}$ is small then the value of $|\ln(\Gamma/\Gamma(\Phi_b))|/\Gamma$ is very small and the accuracy of the determination of $\tilde{\beta}$ on the base of ΔF is very high. The estimate for the error of the determination of $\tilde{\beta}$ can be written as $\Delta\tilde{\beta}/\tilde{\beta} \leq (u_e(\tilde{\beta}) - u_e|_{\tilde{\beta}=0})/u_c(\tilde{\beta})$. Taking into account that $\tilde{\beta} \to 0$, $u_e \to const$, $\Gamma \sim u_c(\tilde{\beta})$ one can see that the error of $3\ln(\Gamma/\Gamma(\Phi_b))/\Gamma$ is grater than the error of determination of $(u_e(\tilde{\beta}) - u_e|_{\tilde{\beta}=0})/u_c(\tilde{\beta})$.

One can use the iteration methods to improve the results.

2.3.4 The main parameters of the condensation on the solid centers

The short range potential leads to the validity of equation

$$\nu_c \gg \nu_e \quad , \tag{2.3.30}$$

which is more weak than $\nu_c \gg 1$, which is necessary for the macroscopic description of the embryo.

The condition of the equilibrium for the critical embryo is rather local one. If we fill be center of the embryo by the liquid phase the embryo remains critical. So, approximately

$$\nu_c = \bar{\nu}_c - \nu_N \quad , \tag{2.3.31}$$

where $\bar{\nu}_c$ is the number of the homogeneous critical embryo, ν_N is the number of the molecules from equation

$$v_l \nu_N = \frac{4\pi r^3}{3} \quad , \tag{2.3.32}$$

where r is the radius of the solid center. The natural condition of the applicability of the two last equations is the validity of the inequality $\bar{\nu}_c - \nu_N \gg 1$. For Γ one can get

$$\Gamma = \frac{\zeta}{\zeta + 1}(\bar{\nu}_c - \nu_N - \nu_e) \quad , \tag{2.3.33}$$

which can be reduced to

$$\Gamma = \frac{\zeta}{\zeta + 1}(\bar{\nu}_c - \nu_N) \quad . \tag{2.3.34}$$

Taking into account the expression for $\bar{\nu}_c$:

$$\bar{\nu}_c = (\frac{2a}{3\ln(\zeta + 1)})^3 \quad , \tag{2.3.35}$$

one can integrate (2.3.34) and get expression for $\Delta F(\zeta)$:

$$\Delta F(\zeta) = \frac{a}{3}(\frac{2a}{3\ln(\zeta + 1)})^2 + \nu_N \ln(\zeta + 1) + const \quad . \tag{2.3.36}$$

Having presented the expression for ΔF as

$$\Delta F(\zeta) = \frac{\ln(\zeta + 1)}{2}(\bar{\nu}_c + 2\nu_N) + const \quad , \tag{2.3.37}$$

determine the constant of the integration. If it is possible to apply (2.3.34) for ν_N near to $\bar{\nu}_c$ then the constant of the integration can be determined from the condition $\Delta F|_{\nu_N = \bar{\nu}_c} = 0$ and is equal to $a\nu_N^{2/3}$.

One can approximately consider $\Delta\nu_e = 1$, $\Delta\nu_c = \Delta\bar{\nu}_c$, $\nu_c = \bar{\nu}_c - \nu_N$.

The results of the iteration procedure can be applied here also. One can find $\ln(\Phi_* + 1)$ on the base of ΔF as the root of the cubic equation.

Analyze qualitatively the dependence Φ_* on the intensity of the creation of the supersaturation. Introduce the value of Φ_b which corresponds to the boundary of the macroscopic description of the embryo or to the barrier character of the condensation. The approximation for

$f_s(\Phi_b)$ will be the following

$$f_s(\Phi_*) = f_s(\Phi_b)\exp\{-\frac{a}{3}[(\frac{2a}{3\ln(\Phi_*+1)})^2 - (\frac{2a}{3\ln(\Phi_b+1)})^2] - \nu_n(\ln(\Phi_*+1)-\ln(\Phi_b+1))\} \quad . \tag{2.3.38}$$

The argument of the exponent can be transformed as

$$-\frac{a}{3}[(\frac{2a}{3\ln(\Phi_*+1)})^2 - (\frac{2a}{3\ln(\Phi_b+1)})^2] - \nu_n(\ln(\Phi_*+1)-\ln(\Phi_b+1)) \approx [\bar{\nu}_c(\Phi_b)-\nu_N]\ln(\frac{\Phi_*+1}{\Phi_b+1}) \quad . \tag{2.3.39}$$

Then for $f_s(\Phi_*)$ one can get

$$f_s(\Phi_*) = f_s(\Phi_b)(\frac{\Phi_*+1}{\Phi_b+1})^{\bar{\nu}(\Phi_b)-\nu_N} \quad . \tag{2.3.40}$$

With the help of the approximation $H'(h)$ for the function $H(h)$ one can get

$$\frac{c}{c(\Phi_b)} \sim [\frac{\Phi_*+1}{\Phi_b+1}]^{\bar{\nu}_c(\Phi_b)-\nu_N} \quad , \quad h_b \le 1 \quad , \quad h \le 1 \quad ,$$
$$[\frac{c}{c(\Phi_b)}]^4 \sim [\frac{\Phi_*+1}{\Phi_b+1}]^{\bar{\nu}_c(\Phi_b)-\nu_N} \quad , \quad h_b \ge 1 \quad , \quad h \ge 1 \quad , \tag{2.3.41}$$

where

$$H(h_b) = \frac{f_s(\Phi_b)}{c(\Phi_b)} \quad ,$$
$$h_b = h(c(\Phi_b)) \quad .$$

If $\Phi(t) = At$, then

$$A \sim [\frac{\Phi_*+1}{\Phi_b+1}]^{\bar{\nu}_c(\Phi_b)-\nu_N} \quad , \quad h_b \le 1 \quad , \quad h \le 1 \quad ,$$
$$A^4 \sim [\frac{\Phi_*+1}{\Phi_b+1}]^{\bar{\nu}_c(\Phi_b)-\nu_N} \quad , \quad h_b \ge 1 \quad , \quad h \ge 1 \quad . \tag{2.3.42}$$

Equation (2.3.36) is valid not only in the case of the short range potential. It is valid for the heterogeneous center of the arbitrary nature when the supersaturation is small and ν_c is very big. Then one can use the last two expressions. For Φ_b one has to take the value of the supersaturation which corresponds to the disappearing of the influence of the center on the surface layer of the critical embryo. æ

2.4 Further evolution of the system

2.4.1 Monodisperce approximation

After the final of PIFD the evolution of the system is determined only by the first three momentums of the spectrum and the number of the droplets which is proportional to the zero momentum of the spectrum.

The contributions into the evolution from these momentums are changed only due to the external conditions. For the total number of the droplets one can get

$$N = V_* N(\infty)/V \quad . \tag{2.4.1}$$

Substituting the second approximation for $N(\infty)$ one can get

$$N = \frac{V_*}{V}\eta(-\infty)[1 - \exp(-\frac{1}{h})] \quad . \tag{2.4.2}$$

The balance equation can be written in the closed system as

$$\Phi = \zeta + \frac{\Phi + 1}{\Phi_* + 1}\sum_{i=0}^{3}\hat{g}_i z^{3-i}\frac{3!(-1)^i}{i!(3-i)!} \tag{2.4.3}$$

and in the open system (the volume is fixed, the temperature is fixed, there is the homogeneous source of the vapor) as

$$\Phi = \zeta + \sum_{i=0}^{3}\hat{g}_i z^{3-i}\frac{3!(-1)^i}{i!(3-i)!} \quad . \tag{2.4.4}$$

When z is great then in the balance equation the main term is $\hat{g}_0$. One can neglect all terms except the mentioned one when z is greater than $\Delta_{\pm}x$.

Consider the last two equations when $t > t_*$. From $z \leq \Delta x$ it follows that the relative quantity of the substance in the droplets is small at t_*.

The value of g grows rapidly but due to the big value of Γ the value g has the same order as Φ_* has only when z essentially exceeds Δx. So, until z isn't greater than Δx one can neglect all terms in the sums in the two last equations. One can also leave $\hat{g}_0 z^3$ as far as it is small. The relative error of such substitution is great but one changes the negligible values. So, the monodisperse approximation, i.e. $\hat{g}_0 z^3$ instead of the sums, is valid for all z. The balance equation will be the following

$$\zeta = \Phi - \frac{\Phi + 1}{\Phi_* + 1} \frac{N(\infty)}{n_{\infty *}} z^3 \tag{2.4.5}$$

for the closed system and

$$\zeta = \Phi - \frac{N(\infty)}{n_\infty} z^3 \tag{2.4.6}$$

for the open system.

This simplifies the consideration but isn't necessary.

With the number of the droplets from the second approximation one can get

$$\zeta = \Phi - \frac{\Phi + 1}{\Phi_* + 1} \frac{\eta(-\infty)}{n_{\infty\ *}} (1 - \exp(-\frac{1}{h})) z^3 \quad , \tag{2.4.7}$$

$$\zeta = \Phi - \frac{\eta(-\infty)}{n_{\infty\ *}} (1 - \exp(-\frac{1}{h})) z^3 \quad . \tag{2.4.8}$$

According to the definition of h one can express $\eta(-\infty)$ via h and get

$$\zeta = \Phi - \frac{\Phi + 1}{\Phi_* + 1} \frac{\Phi_*}{6\Gamma} h (1 - \exp(-\frac{1}{h})) c^3 z^3 \quad , \tag{2.4.9}$$

$$\zeta = \Phi - \frac{\Phi_*}{6\Gamma} h (1 - \exp(-\frac{1}{h})) c^3 z^3 \quad . \tag{2.4.10}$$

After the transformation from ζ to dz/dt the last two equations will be the following

$$\frac{dz}{dt} = \frac{\alpha}{S(\Phi_*)\tau_*} (\Phi - \frac{\Phi + 1}{\Phi_* + 1} \frac{\Phi_*}{6\Gamma} h (1 - \exp(-\frac{1}{h})) c^3 z^3) \quad , \tag{2.4.11}$$

$$\frac{dz}{dt} = \frac{\alpha}{\tau} (\Phi - \frac{\Phi_*}{6\Gamma} h (1 - \exp(-\frac{1}{h})) c^3 z^3) \quad . \tag{2.4.12}$$

2.4.2 Collapse of the system. Asymptotical period

Consider the times when

$$\frac{|\Phi - \Phi_*|}{\Phi_*} \ll 1 \quad . \tag{2.4.13}$$

The balance equation will be the following

$$\zeta = \Phi_*(1 - \frac{1}{6\Gamma}h(1 - \exp(-\frac{1}{h}))c^3z^3) \quad , \tag{2.4.14}$$

or

$$\frac{dz}{dt} = \frac{\alpha}{\tau_*}\Phi_*(1 - \frac{1}{6\Gamma}h(1 - \exp(-\frac{1}{h}))c^3z^3) \quad . \tag{2.4.15}$$

The initial condition will be $z|_{t=t_*} = 0$. The solution is

$$\frac{t - t_*}{t_r} = \ln[\frac{(\frac{z^2}{z_r^2} + \frac{z}{z_r} + 1)^{1/2}}{1 - \frac{z}{z_r}}] + \sqrt{3}\arctan(\frac{2z}{\sqrt{3}z_r} + \frac{1}{\sqrt{3}}) - \frac{\pi}{2\sqrt{3}} \quad , \tag{2.4.16}$$

where

$$z_r = [\frac{6\Gamma}{h(1 - \exp(-\frac{1}{h}))}]^{1/3}\frac{1}{c} \quad , \tag{2.4.17}$$

$$t_r = [\frac{6}{\Gamma^2 h(1 - \exp(-\frac{1}{h}))}]^{1/3}\frac{t_*}{3m} \tag{2.4.18}$$

One can extract three stages. The condition $\zeta \simeq \zeta_*$ will extract the initial stage. As it follows from (2.4.14), (2.4.16) it is restricted by $-\Delta_- t \leq t - t_* \leq 3t_r/2$. At the initial stage

$$z = \frac{m\Gamma}{c}\frac{t - t_*}{t_*} \quad , \quad -\Delta_- t \leq t - t_* \leq \frac{3}{2}t_r \quad . \tag{2.4.19}$$

After the initial stage there will be the collapse of the system. It begins at $t - t_* \simeq 3t_r/2$ and finishes at $t - t_* \simeq 3t_r$. If $|\Phi - \Phi_*| \ll \Phi_*$ is valid when $t - t_* \geq 3t_r$ the solution can be reduced to

$$z = z_r[1 - \sqrt{3}\exp(\frac{\pi}{2\sqrt{3}})\exp(-\frac{t - t_*}{t_r})] \quad , \tag{2.4.20}$$

$$\zeta = 3\sqrt{3}\exp(\frac{\pi}{2\sqrt{3}})\exp(-\frac{t-t_*}{t_r})\Phi_* \quad . \tag{2.4.21}$$

The final stage begins at $t - t_* \simeq 3t_r$. The last two equations only when $|\Phi - \Phi_*| \ll \Phi_*$. It is valid when

$$[\frac{6}{\Gamma^2 h(1-\exp(-\frac{1}{h}))}]^{1/3} \ll 1 \quad . \tag{2.4.22}$$

The equation (2.4.21) shows that at $t-t_* \simeq 3t_r$ the value of ζ is small in comparison with Φ. It allows to construct the asymptotic expansions taking into account the growth of the ideal supersaturation. One can come to

$$z = z_r(\frac{\Phi_*+1}{\Phi_*})^{1/3}(\frac{\Phi-\zeta}{\Phi+1})^{1/3} \quad . \tag{2.4.23}$$

After the substitution $\Phi-\zeta \approx \Phi$ one can come in the zero approximation to

$$z = z_r(\frac{\Phi_*+1}{\Phi_*})^{1/3}(\frac{\Phi}{\Phi+1})^{1/3} \quad , \tag{2.4.24}$$

$$\zeta = \frac{cz_r}{3\Gamma}(\frac{\Phi_*+1}{\Phi_*})^{1/3}(\frac{\Phi}{\Phi+1})^{4/3}(\frac{\Phi_*}{\Phi})^{(m+1)/m}\frac{n_{\infty *}}{n_\infty} \quad . \tag{2.4.25}$$

The value of ζ decreases in the process of the isothermal compression and in the case of the isochoric cooling. In the case of adiabatic compression it decreases when

$$0 < m \leq \frac{1}{j} \quad . \tag{2.4.26}$$

Asymptotic equations (2.4.24), (2.4.25) allow to determine all characteristics of the condensation process. The time of the transformation to the process of the coalescence is given by

$$t_{cond} \approx t_*[(\frac{cz_r}{3\Gamma(\exp(\frac{2a}{z_r-\Delta_+ x})-1)})^d - 1] \quad , \tag{2.4.27}$$

where $d = 1/(m+1)$ in the case of isothermal compression, $d = 1$ in the case of isolhoric cooling, $d = 1/(1-mj)$ in the case of adiabatic compression.

In the materially open system one can see instead of (2.4.23) the following equation

$$z = \frac{(\Phi-\zeta)^{1/3}}{N(\infty)^{1/3}}n_\infty^{1/3} \quad . \tag{2.4.28}$$

Having put $\Phi - \zeta \approx \Phi$ one can get in the zero approximation

$$z = \frac{\Phi(t)^{1/3} n_\infty^{1/3}}{N(\infty)^{1/3}} \quad , \tag{2.4.29}$$

$$\zeta = \frac{\tau}{\alpha}(\frac{n_\infty}{N(\infty)})^{1/3}\frac{m}{3}(\frac{t}{t_\infty})^{\frac{m}{3}-1}t_\infty^{-1} \quad . \tag{2.4.30}$$

After the substitution of ζ into (2.4.28) one can get the expressions for z and for ζ in the second approximation. One can construct the whole asymptotic seria in this manner.

For ζ to decrease it is necessary that $\Phi(t)$ grows more slowly than t^3. For t_{cond} one can get the following expression

$$(\frac{t_{cond}+t_*}{t_\infty})^{\frac{m}{3}-1} = \frac{\alpha}{\tau}(\frac{N(\infty)}{n_\infty})^{1/3}\frac{3}{m}t_\infty(\exp(\frac{2a}{z-\Delta_+ x}) - 1) \quad . \tag{2.4.31}$$

It can be reduced to

$$t_{cond} = -t_* + t_\infty(6\frac{\alpha}{\tau}(\frac{N(\infty)}{n_\infty})^{2/3}at_\infty)^{\frac{3}{2m-3}} \quad . \tag{2.4.32}$$

It follows that the coalescence is possible when $\Phi(t)$ grows more slowly than $t^{3/2}$.

* * *

The generalization for the arbitrary regime of the substance exchange can be made by the same approach.

* * *

The short character of the stage of collapse is very important in the investigation of stochastic spread of the size spectrum. Due to the stochastic character of collisions of the molecules with the embryo the growth of the embryo will be stochastic also. In the diffusion regime as well as in the nonisothermal effects there appears some compensation which regulates the rate of growth. In the free molecular regime the stochastic spread plays some more important role. But one can show that it is small.

The diffusion is going alon ν which doesn't act on the balance of the substance. The influence can be observed only by the variation of the size of the embryo which leads to the variation of the rate of growth. In the variable $\nu^{1/3}$ the influence of this effect is rather small, one can simply establish the corrections to the already constructed solution.

Due to the absolutely stochastic character of the process one can present the distribution of droplets on the number of the molecules. It corresponds to the distribution of the number of the ideal gas molecules in the volume $v_v L$, where v_v is the mean volume for the molecule in the vapor, L is the mean number of the molecules in the subsystem. This number is chosen as the total number of the interactions in the whole evolution of the embryo of the given size[17].

At the stage of the collapse the essential spread of the spectrum is impossible due to the short character of this stage. At the asymptotic stage this effect is important. But one can rewrite the analogous equation also in the case of stochastic consumption. The corrections are the obvious ones. The reason is the strong balance connection which takes place at the asymptotic stage.

2.4.3 The further evolution at the small number of the heterogeneous centers. The period of the increase of the supersaturation.

When $\eta(-\infty)$ decreases the value h becomes too small and the conditions (2.4.22) will be violated. In the case of the isothermal compression the balance equation can be written as

$$\frac{\tau_*}{\alpha}\frac{dz}{dt} + \frac{\Phi+1}{\Phi_*+1}\frac{N(\infty)}{n_{\infty\,*}}z^3 = \Phi \quad , \tag{2.4.33}$$

and in the open system it can be written as

$$\frac{\tau}{\alpha}\frac{dz}{dt} + \frac{N(\infty)}{n_{\infty\,*}}z^3 = \Phi \tag{2.4.34}$$

which is the worst case for the methods described later. So we shall analyze this situation.

Under the isochoric cooling the balance equation will be the following

$$\frac{\tau_*}{\alpha}\frac{dz}{dt} + \frac{N(\infty)}{n_{\infty\,*}}z^3 = \Phi\frac{\Phi_*+1}{\Phi+1} \tag{2.4.35}$$

and can be reduced to the case of the open system with slightly another source. In this case the further description will be better than in the open system.

[17] This number depends on the behavior of the supersaturation and can be found in some approximation. This leads to some iteration process for the precise solution.

The case of adiabatic expansion due to $j \ll 1$ is rather analogous to the case of isochoric cooling. In any case the precision in this case will be higher than in the case of the open system. So we shall consider the case of the open system.

Suppose that $\Phi(t)$ can be linearized at this period

$$\Phi(t) = \Phi_* + A(t - t_*) \quad , \quad A \simeq const \quad . \tag{2.4.36}$$

The coefficient A can be included in τ. Having transmitted the zero moment of time to t_* one can come to

$$\tau \frac{dz}{dt} = \Phi_* + At - \frac{\eta_{tot}}{n_\infty} z^3 \quad , \tag{2.4.37}$$

$$z|_{t=0} = 0 \quad .$$

After transformations from z to

$$z \to \frac{n_\infty^{2/5} A^{1/5} \tau^{1/5}}{\eta_{tot}^{2/5}} z$$

and from t to

$$t \to \frac{\tau^{3/5} n_\infty^{1/5}}{A^{2/5} \eta_{tot}^{1/5}} t$$

one can get

$$\frac{dz}{dt} = \gamma + t - z^3 \quad , \tag{2.4.38}$$

where

$$\gamma = \frac{\Phi_* \eta_{tot}^{1/5}}{A^{3/5} \tau^{3/5} n_\infty^{1/5}} \tag{2.4.39}$$

with the previous initial condition.

Construct the seria of iterations. One can show that the solution grows to infinity and dz/dt has the maximum at some moment t_m (index m marks the value at this moment). It is necessary to construct approximations for $z(t)$ and $\zeta(t)$ at $[0, t_m]$.

Consider the iterations for $z(t)$, $\hat{\Phi} = dz/dt$, $\hat{\Psi} = d^2z/dt^2$

$$\hat{\Phi}_i \equiv (\frac{dz}{dt})_i = t - z_{i-1}(t)^3 + \gamma \ , \quad i = 1, 2, 3 \quad ,$$

$$\hat{\Psi}_i \equiv (\frac{d^2z}{dt^2})_i = 1 - 3 z_{i-1}(t)^2 (\frac{dz}{dt})_{i-1} \quad , n \tag{2.4.40}$$

$$z_i = \int_0^t \hat{\Phi}_i(t') dt' \quad .$$

Index i will mark the number of the iteration. The initial approximation will be the following

$$\Phi_0 = 0 < \Phi(t) \quad .$$

So, one can come to

$$\begin{aligned} &\hat{\Phi}_0 < \hat{\Phi}_2 < ... < \hat{\Phi}_{2i} < ... < \hat{\Phi} < ... < \hat{\Phi}_{2i+1} < ... < \hat{\Phi}_3 < \hat{\Phi}_1 \quad , \\ &\hat{\Psi}_2 < \hat{\Psi}_4 < ... < \hat{\Psi}_{2i} < ... < \hat{\Psi} < ... < \hat{\Psi}_{2i+1} < ... < \hat{\Psi}_3 < \hat{\Psi}_1 \\ &z_0 < z_2 < ... < z_{2i} < ... < z < ... < z_{2i+1} < ... < z_3 < z_1 \quad . \end{aligned} \tag{2.4.41}$$

Due to (2.4.40) one can get

$$\frac{dz_i}{dt} = (\frac{dz}{dt})_i = \hat{\Phi}_i \quad ,$$

$$\frac{d^2 z_i}{dt^2} = (\frac{d^2 z}{dt^2})_i = \hat{\Psi}_i \quad ,$$

which allow to get

$$\begin{aligned} \frac{d|z - z_{2i}|}{dt} &= \hat{\Phi} - \hat{\Phi}_{2i} > 0 \quad , \\ \frac{d|z - z_{2i+1}|}{dt} &= \hat{\Phi}_{2i+1} - \hat{\Phi} > 0 \quad , \\ \frac{d|\hat{\Phi} - \hat{\Phi}_{2i}|}{dt} &= \hat{\Psi} - \hat{\Psi}_{2i} > 0 \quad , \\ \frac{d|\hat{\Phi} - \hat{\Phi}_{2i+1}|}{dt} &= \hat{\Psi}_{2i+1} - \hat{\Psi} > 0 \quad . \end{aligned} \tag{2.4.42}$$

One can also show that

$$\frac{d|\hat{\Psi} - \hat{\Psi}_{2i}|}{dt} = \frac{d^3 z}{dt^3} - \frac{d^3 z_{2i}}{dt^3} > 0 \quad ,$$

$$\frac{d|\hat{\Psi} - \hat{\Psi}_{2i+1}|}{dt} = \frac{d^3 z_{2i+1}}{dt^3} - \frac{d^3 z}{dt^3} > 0 \quad .$$

The iterations for $\hat{\Phi}$, $\hat{\Psi}$, z have the polynomial form on t. This allows to calculate all iterations. The first two ones are

$$\hat{\Phi}_1 = t + \gamma \quad ,$$

$$z_1 = \frac{t^2}{2} + \gamma t \quad ,$$

$$\hat{\Psi}_1 = 1 \quad ,$$

$$\hat{\Phi}_2 = t + \gamma - (\frac{t^2}{2} + \gamma t)^3 \quad ,$$

$$\hat{\Psi}_2 = 1 - 3(t+\gamma)(\frac{t^2}{2} + \gamma t)^2 \quad ,$$

$$z_2 = \gamma t + \frac{t^2}{2} - \gamma^3 \frac{t^4}{4} - 3\gamma^2 \frac{t^5}{10} - \gamma \frac{t^6}{8} - \frac{t^7}{56} \quad .$$

Estimate the velocity of convergence of the iterations for $\hat{\Phi}$. According to (2.4.42) the error of the definition of $\hat{\Phi}$ grows in time. So, we shall estimate it at t_m. After the differentiation (2.4.38) at t_m leads to

$$1 = 3z_m^2 \frac{dz}{dt}|_{t=t_m} \quad . \tag{2.4.43}$$

Due to (2.4.38) one can rewrite (2.4.43) in the following form

$$1 = 3z_m^2(\gamma + t_m) - 3z_m^5 \quad . \tag{2.4.44}$$

Introduce $\hat{\alpha}$ as

$$z^3(t) = \hat{\alpha}(t+\gamma) \quad . \tag{2.4.45}$$

The greater $\hat{\alpha}$ is the greater is the difference between the iteration and the precise $\hat{\Phi}(t)$. Consider $\hat{\alpha}_m = \hat{\alpha}(t_m)$. For $t < t_m$ there is $\hat{\alpha}(t) < \hat{\alpha}_m$.

The last equation can be rewritten as

$$1 = 3(\gamma + t_m)^{5/3}(\hat{\alpha}_m^{2/3} - \hat{\alpha}_m^{5/3}) \quad . \tag{2.4.46}$$

It is necessary to prove that $L = t_m + \gamma$ grows when γ grows:

- 1. There exists the point with $dL/dt = 0$.

  Suppose that L decreases when γ increases. Due to $t_m > 0$ the value of L can not only decrease. So the necessary point exists. Then for one $L(\gamma)$ we have the different values of γ.

- 2. For $\hat{\zeta}_m$, z_m one can come to the following system

$$\begin{gathered} L = \hat{\zeta}_m + z_m^3 \quad , \quad \hat{\zeta}_m \equiv (\frac{dz}{dt})_m \quad , \\ 1 = 3z_m^2 \hat{\zeta}_m \end{gathered} \tag{2.4.47}$$

Consider these equations as two functions $\hat{\zeta}_m$ on z_m. These curves cross not more than two times. If $L > L_{cr}$, they cross two times, if $L = L_{cr}$, they touch one another one time, if $L < L_{cr}$, they have no common points.

- 3. For L_{cr} one can have

$$z_{cr} = (\frac{2}{9})^{1/5} \quad , \quad L_{cr} = \frac{1}{3}(\frac{2}{9})^{-2/5} + (\frac{2}{9})^{3/5} \approx 1.014 \quad . \qquad (2.4.48)$$

  For $L > L_{cr}$ there are two families of the roots z:

  the first family z_1 is less than z_{cr},

  the second family z_2 is greater than z_{cr}.

- 4. Consider the asymptotic behavior of the roots.

  When $\gamma \to \infty$, $L \to \infty$, $z_1 \to \infty$, $z_2 \to 0$ the first family is impossible as far as $t_m > 0$, $\hat{\zeta}_m > \gamma \to \infty$.

  So, only the second family is possible.

- 5. The trajectories $\hat{\zeta}$ under the unique choice of the zero point of time can not cross. So, according to (2.4.47) the value of z decreases when γ increases. Then $min_\gamma z_m = z_m(\gamma = 0)$.

- 6. Fulfill the calculations.

  A). $z_m(\gamma = 0) < z_{cr}$.

  B).$L(\gamma = 0) > 1.059$.

  Then z is less than z_m and must be from the family of the solutions where when L increases the value of z_m decreases. Then L can not decrease when γ increase.

If one can show that

$$\tilde{f}(\hat{\alpha}_m) \equiv \hat{\alpha}_m^{2/3} - \hat{\alpha}_m^{5/3}$$

is the monotonous function of $\hat{\alpha}_m$, then the maximum of $\hat{\alpha}_m$ is attained at the minimal $t_m + \gamma$ or at the minimal γ.

Differentiate $\tilde{f}(\hat{\alpha}_m)$

$$3\frac{d\tilde{f}}{d\hat{\alpha}_m} = 2\hat{\alpha}_m^{-1/3} - 5\hat{\alpha}_m^{2/3} \quad .$$

At $[0,1]$ when $\hat{\alpha}_m < 2/5$ the derivative is the positive and when $\hat{\alpha}_m > 2/5$ the derivative is the negative.

Seek for the estimate for $\hat{\alpha}_m$ at $\gamma = 0$. Take into account that

$$t_{m\ 2i+1} > t_m > t_{m\ 2i} \quad ,$$

where $t_{m\ i}$ is defined according to

$$\hat{\Psi}_i(t_{m\ i}) = 0 \quad .$$

Then

$$\hat{\alpha}_m(\gamma = 0) = \frac{z^3}{t_m} < \frac{\tilde{z}^3_{2i-1}(t_{m\ 2i+1})}{t_{m\ 2i}} \quad . \tag{2.4.49}$$

After the calculations for $i = 1$ one can come to $\hat{\alpha}_m < 0.3$. At $[0, 0.3]$ the function $\tilde{f}(\hat{\alpha}_m)$ grows monotonically when $\hat{\alpha}_m$ grows. So, the interval $[0, 0.3]$ contains the region of the variation of the parameter $\hat{\alpha}$. Due to (2.4.46) the increase of $t_m + \gamma$ leads to the increase of $\tilde{f}(\hat{\alpha}_m)$ and to the increase of $\hat{\alpha}_m$. So the maximal quantity of the substance in the droplets is attained when $t = t_m$ if $\gamma = 0$.

Introduce

$$\Delta_{i,i+1} = \frac{|max_t\hat{\Phi}_i - max_t\hat{\Phi}_{i-1}|}{max_t\hat{\Phi}_i} \tag{2.4.50}$$

for the error of the iterations. Due to (2.4.41) the error

$$\Delta_i = \frac{|max_t\hat{\Phi} - max_t\hat{\Phi}_i|}{max_t\hat{\Phi}} \tag{2.4.51}$$

is less than $\Delta_{i,i-1}$. The value $\Delta_{i,i-1}$ attains maximum when $\gamma = 0$. The calculations give $\Delta_2 < 0.041$, $\Delta_2 < 0.00868$.

In the diffusion regime it is possible to calculate analytically only the first two iterations. The second iteration doesn't come to the maximum. Then one can reconsider the initial approximation. The old first iteration has the maximum. Define the initial approximation as the ideal supersaturation until the level of the already obtained maximum and as the constant equal to this level later. Calculate the iterations again. Then the second iteration can be calculated analytically and has the maximum. The relative error in the maximum is less than 0.008.

2.4.4 The methods for the description of the decrease of the supersaturation.

The asymptotic equations remain the same also in this case. So, one has to investigate only the evolution until the asymptotic period. The

difficulty lies in the fact that the approximation $\Phi \approx \Phi_*$ can not lead to the precise results.

The balance equation can be written as

$$z_{tot}^3 = \frac{dz}{dt} + z^3 \quad , \tag{2.4.52}$$

where z_{tot} is defined as

$$z_{tot} = \hat{L}(t)^{1/3} \quad , \quad \hat{L}(t) = t + \gamma \quad . \tag{2.4.53}$$

Then for $\hat{y} = z/z_{tot}$ one can get

$$z_{tot}\frac{d\hat{y}}{dt} + \hat{y}\frac{dz_{tot}}{dt} = z_{tot}^3(1 - \hat{y}^3) \quad . \tag{2.4.54}$$

When $t \to \infty$ the value of $\hat{y}$ goes to 1. Then one can neglect at the initial period $\hat{y}dz_{tot}/dt$ and get

$$\frac{d\hat{y}}{dt} = z_{tot}^2(1 - \hat{y})^3 \quad , \tag{2.4.55}$$

which allows the analytical solution

$$\int_{y_m}^{y} \frac{d\hat{y}'}{1 - \hat{y'}^3} = \int_{t_m}^{t} z_{tot}^2 dt \quad . \tag{2.4.56}$$

For big t

$$\frac{\hat{y}\frac{dz_{tot}}{dt}}{\frac{d\hat{y}}{dt}z_{tot}} \to \frac{9}{5}t^{5/3}$$

and the neglected term is great. Then one can put this asymptotic relation in the equation and come to

$$(1 + \frac{9}{5}t^{5/3})\frac{d\hat{y}}{dt} = z_{tot}^2(1 - \hat{y}^3) \quad , \tag{2.4.57}$$

which can be solved analytically. The combination of the solutions (2.4.55) and (2.4.57) also can be considered as the good approximation for the evolution.

One can extract in the decrease of ζ/Φ two factors: the increase of Φ and the decrease of ζ. When the first factor is the main one then one can approximately say that

$$t - t_m = (z - z_m)/(\frac{dz}{dt})_m$$

and get

$$(z - z_m)/(\frac{dz}{dt})_m + \hat{\zeta}_m = \frac{dz}{dt} + z^3 \quad . \tag{2.4.58}$$

The last equation can be easily solved

$$\int_{z_m}^{z} [(z - z_m)/(\frac{dz}{dt})_m + \hat{\zeta}_m - z^3]^{-1} dz = t - t_m \quad . \tag{2.4.59}$$

If the second factor is the main one then one can neglect $\Phi - \hat{\zeta}_m$ in comparison with $\hat{\zeta}_m$. As far as

$$(z - z_m)/(\frac{dz}{dt})_m < (t - t_m) = \Phi - \hat{\zeta}_m \quad , \tag{2.4.60}$$

the term $(z - z_m)/(dz/dt)_m$ is negligible in comparison with $\hat{\zeta}_m$ and it can be introduced in the balance equation in this case also. So, (2.4.58) can be applied also in this situation.

2.5 Global dependencies in the condensation

In 1925 the experimental law for the radius of the droplets in the system was established [29] by von Wiemarn. We are going to give the derivation of this law. We shall consider the mean radius R of the droplets in the system. The law of von Weimarn can be presented in the following form:

$$\frac{R(\zeta_1)}{R(\zeta_2)} = (\frac{\zeta_1}{\zeta_2})^w \quad , \tag{2.5.1}$$

where ζ_1 and ζ_2 are two values of the supersaturation (defined as the ratio of the molecule number density of the existing vapor to the molecules number density in the saturated vapor), w is some constant.

The necessary conclusions from the previous consideration are the following ones

- (j) The total number of the droplets is proportional to (the free molecular regime is considered)

$$N(\zeta) \sim f_*^{3/4} \quad , \tag{2.5.2}$$

where f_* is the amplitude of the distribution on the linear size.

- (jj) All droplets are formed during the rather short period then they attain some size rather quickly. Then their size will be approximately constant during the rather long period of time.
- (jjj) The embryos can be considered as the super critical embryos.
- (jjjj) The spectrum has the monodisperse form (after the end of the collapse).
- (jjjjj) One can use the quasi stationary approximation.

According to (j) one can approximately get

$$\frac{N(\zeta_1)}{N(\zeta_2)} = \exp(\frac{3}{4}(-F_{hom}(\zeta_1) + F_{hom}(\zeta_2))) \quad . \tag{2.5.3}$$

Then the characteristic scale of the region of ζ corresponding to the increase of N from the negligible value up to the "smog" value is given by

$$|F_{hom}(\zeta_1) - F_{hom}(\zeta_*)| \leq (3...4) \quad , \tag{2.5.4}$$

where ζ_* is the middle of this region.

In this region the following approximation

$$F_{hom}(\zeta_2) - F_{hom}(\zeta_1) \approx \nu_c \ln(\frac{\zeta_2}{\zeta_1}) \tag{2.5.5}$$

is valid.

Taking into account the law of growth

$$\frac{d\nu^{1/3}}{dt} \sim \zeta - 1 \tag{2.5.6}$$

in the leading term (jjj), one can get due to (jj) and (jjj) the mean radius R from the balance equation

$$N\frac{4\rho_{liquid}\pi}{3}R^3 = \zeta - 1 \quad , \tag{2.5.7}$$

where ρ_{liquid} is the molecules number density in the liquid.

The combination of (2.5.3) and (2.5.7) gives

$$(\frac{R(\zeta_1)}{R(\zeta_2)})^3 = \frac{\zeta_1 - 1}{\zeta_2 - 1}(\frac{\zeta_2}{\zeta_1})^{3\nu_c/4} \tag{2.5.8}$$

in the whole region (2.5.4). According to the essential value of ν_c one can leave only the power term

$$\frac{R(\zeta_1)}{R(\zeta_2)} = (\frac{\zeta_2}{\zeta_1})^{\nu_c/4} \quad . \tag{2.5.9}$$

In the heterogeneous condensation when the vapor consumption is essential all considerations are quite analogous. One have to substitute ν_c by $\nu_c - \nu_e$. The consideration for the other power like dependences of the velocity of the droplets growth is quite analogous. As the result one can get the law of the mentioned form, but the power will be $\alpha\nu_c/(1+\alpha)$ instead of $\nu_c/4$.

The form of the law doesn't depend on the form of the external conditions. The same result will be under the stabilization of the external conditions in some moment of time. Certainly, in the dynamic conditions the final supersaturation has to be corrected and it grows in time. So, the final radius also grows in time but rather slowly.

The mentioned property is the consequence of the global law of "inertion of the characteristics of the phase transition": **When the maximum supersaturations in the system are the same then all main characteristics of the phase transition have one and the same order under all external conditions ensuring the growth or under the stabilization of the ideal supersaturation.**

This law can be justified in all situations considered later. Also one can construct the solution under the stabilization of the external conditions by the same methods.

This law can be spread over the existence of profiles of the density and temperature around the droplets and over the arbitrary given regime of the droplets growth.

There is some universality concerning the change of the regime of the substance exchange but it has a special meaning and will be discussed in the chapter six.

2.6 Non stationary effects of the condensation

In the last years the process of the nucleation was considered in the non stationary way by Schneidman [65]. The measure of the non stationary

effects can be considered as

$$n = -\frac{t_s}{2}\frac{\partial}{\partial t}F_c \quad , \tag{2.6.1}$$

where the time t_s characterizes the relaxation to the stationary state.

As far as we are going to get the very strong inequalities one can use the homogeneous value for the free energy. The consideration of the cited papers describes the situation when n doesn't vary essentially during $\frac{t_s}{2}$. It allows to investigate the quasi stationary distribution on parameter n.

This approach seems doubtful as far as the maximum value of the embryos is formed in the neighborhood of the maximum of the supersaturation where n goes to zero. Consider the process of the homogeneous condensation[18].

The thermodynamic description is valid when

$$\nu_c \gg 1 \quad . \tag{2.6.2}$$

Then for the rate of nucleation I one can get the following expression

$$\ln I \sim -F_c \quad . \tag{2.6.3}$$

The dimensionless surface tension a is small only in near the second order phase transition. Then $F_c \gg 1$, $dF_c/d\zeta \gg 1$. When the supersaturation is changed by $\zeta\nu_c/(\zeta+1)$ the rate of nucleation changes in e times.

Under such a variation the derivative dF_c/dt is approximately constant. Then from the constant value of dF_c/dt the constant value for $d\zeta/dt$ follows. In the balance equation

$$\Phi = \zeta + g \quad , \tag{2.6.4}$$

one can estimate g as

$$g \sim I(\Delta t)^4(\frac{d\nu^{1/3}}{dt})^3 \tag{2.6.5}$$

for $\nu \geq (3..5)^3\nu_c$. Here $2\Delta t$ is the duration of PIFD. The regime of the substance exchange if the free molecular one.

One can suppose that the index "*" denotes the values at the moment of the maximum of the supersaturation. This moment is close to the

[18]The index marking the homogeneous character of the process is omitted.

moment of the maximum of the intensity of the droplets formation. Then one can get from the last two equations

$$\frac{d\Phi}{dt} \mid_* \sim I_*(\Delta t)^3 (\frac{d\nu^{1/3}}{dt})^3 \quad . \tag{2.6.6}$$

Then

$$\Delta t \sim g_* / \frac{d\Phi}{dt} \mid_* \quad . \tag{2.6.7}$$

The justification of the disbalanced iterations can be made by the following way. Construct the first iteration formally on the base of the precise value of the nucleation rate until the moment when $g > (\zeta+1)/\nu_c$. Define this moment from equation $g \sim (\zeta + 1)/\nu_c$. It equals to t_*. So, the first and all other iterations as well as the mentioned inequalities and approximations can be applied.

From $g_* \approx (\zeta + 1)/\nu_c$ it follows

$$\Delta t \approx (\zeta + 1)/[\nu_c \frac{d\Phi}{dt} \mid_*] \ , \tag{2.6.8}$$

and (2.6.6) leads to

$$(\frac{d\Phi}{dt} \mid_*)^4 \approx I_* \frac{(\zeta + 1)^3}{\nu_c^3} (\frac{d\nu^{1/3}}{dt})^3 \quad . \tag{2.6.9}$$

The possibility of application of the quasi stationary approximation can be justified by the validity of two inequalities

$$\mid [\frac{dF_c(\Phi)}{dt}]^{-1} \mid \gg \frac{t_s}{2} \quad , \tag{2.6.10}$$

$$\Delta t \gg \frac{t_s}{2} \quad . \tag{2.6.11}$$

According to (2.6.8) these inequalities have the same power. From (2.6.3), (2.6.6), (2.6.8), (2.6.9) one can get

$$\ln(\Delta t / \frac{t_s}{2}) \approx a\nu_c^{2/3}/12 \gg 1 \quad . \tag{2.6.12}$$

The last inequality justifies the necessary inequalities.

* * *

In the explicit construction of the nonstationary description the rate of nucleation begins to depend on the behavior of the free energy at the

small sizes (if we adopt the analytical expansion which is doubtful). In the papers of Schneidman the capillarity approximation was applied also in the region of the small sizes which isn't valid. But in the other case one can not get any solution.

Also one have to stress that even the free energy for the small size would be known the quasi stationary approximation on n can not be used in the real process of the condensation under the dynamic conditions.

* * *

In the heterogeneous condensation the derivation will be absolutely analogous. One has to exclude the case of the total exhaustion of the heterogeneous centers. But in this case the result will be obvious - the spectrum is monodesperse one and the total number of the droplets is equal to the total number of the droplets.

* * *

The analogous consideration can be fulfilled in the case of the stabilization of the ideal supersaturation. One can analytically prove that under the same maximal supersaturations all characteristics of the process of the condensation have one and the same order for all external conditions which ensure the growth of the ideal supersaturation, for the stabilization of the ideal supersaturation and for the situation of the decay[19]. So, all conclusions will be the same.

In the heterogeneous condensation the situation is the same. The variation (which is not so essential) occurs only when the exhaustion of the heterogeneous centers is the reason for the interruption of the formation of the droplets[20].

The nonstationary effects of the condensation can be seen only under the unmonotonuos character of the ideal supersaturation. In the end of this chapter and in the forth chapter it is shown that in the case when one can see the effects of the nonstationarity the ideal supersaturation coincides with the real supersaturation and one has simply to calculate the rate of non stationary nucleation on the base of the given supersaturation. Also it will be shown that there is some compensation in this calculation. One can say that **the scales of the "self-nucleation" have the same orders under the same values of the maximal rate of nucleation**.

[19] Except the situation when all heterogeneous centers are exhausted. Then one has to take instead of the maximal supersaturation the rate of nucelation.

[20] This will be discussed in the chapter six.

One can approximate in the neighborhood of the maximum of the supersaturation the free energy as the linear function of the supersaturation. The big value of $dF_c/d\zeta$ leads to the disappearing of the rate of nucleation when the decrease of the supersaturation is almost negligible.

At PIFD one can put

$$\mid \zeta_{max} - \zeta \mid \leq (dF_c/d\zeta)^{-1} \quad , \tag{2.6.13}$$

where $\zeta_{max} = \zeta(t_{max})$ is the maximal value of the supersaturation.

The square dependence for the supersaturation

$$\zeta = \zeta_{max} + \frac{d^2\zeta/dt^2}{2} \mid_{t_{max}} (t - t_{max})^2 \tag{2.6.14}$$

leads to

$$\Delta t \approx \frac{2}{\mid d^2\zeta/dt^2 \mid_{t_{max}} \alpha \mid)^{1/2}} \quad , \tag{2.6.15}$$

where

$$\alpha = \frac{dF_c}{d\zeta} \quad . \tag{2.6.16}$$

The parameter n goes during the period of the intensive formation of the droplets from $-n_0$ till 0 and from 0 till n_0 where

$$n_0 = \frac{t_s}{2} \frac{\nu_c(\zeta_{max})}{\zeta_{max} + 1} \frac{d^2\zeta}{dt^2} \mid_{t_{max}} \Delta t \quad . \tag{2.6.17}$$

To see the nonstationary effects it is necessary that

$$\mid n_0 \mid \sim 1 \quad . \tag{2.6.18}$$

To use the approximation of the constant value of n it is necessary that

$$\frac{\frac{\partial n}{\partial t} \frac{t_s}{2}}{n} \ll 1 \quad . \tag{2.6.19}$$

But one can see

$$\frac{\partial n}{\partial t} \approx \frac{n}{\Delta t} \tag{2.6.20}$$

and then

$$\frac{\frac{t_s}{2}}{\Delta t} \ll 1 \quad . \tag{2.6.21}$$

The disappearing of the rate of nucleation requires that

$$\frac{\nu_c(\zeta_{max})}{\zeta_{max} + 1} \frac{d^2\zeta}{dt^2} \mid_{t_{max}} \Delta t^2 \sim 1 \quad . \tag{2.6.22}$$

Then

$$n_0 \approx \frac{\frac{t_s}{2}}{\Delta t} \ll 1 \quad , \tag{2.6.23}$$

which is in contradiction with (2.6.18). So, the quasi stationary approximation on the parameter n can not be applied.

One can simplify the model of the evolution in the critical region. The main dependence of the nucleation rate on the supersaturation occurs due to the equilibrium boundary condition at the lower end of the critical region. It can be proved analytically by the transition from ν, t to ν/ν_c, t where the position of the critical region is almost stable. The additional terms appeared in this transition are negligible.

One can put the boundary condition more deep in the precritical region in order to have the fixed condition in time[21].

After the shift of ν (zero point is put to ν_c), rescaling of ν (the new variable will be denoted as y) and rescaling of t one can come in the Fokker-Planck approximation to the following equation for the distribution n_{distr}

$$\frac{\partial n_{distr}}{\partial t} = \frac{\partial}{\partial y} \exp(y^2) \frac{\partial}{\partial y} \frac{n_{distr}}{\exp(y^2)} \quad . \tag{2.6.24}$$

After the transition to the function

$$v = \frac{n_{distr}}{\exp(y^2)} \quad , \tag{2.6.25}$$

one can come to

$$\frac{\partial v}{\partial t} = 2y \frac{\partial v}{\partial y} + \frac{\partial^2 v}{\partial y^2} \quad . \tag{2.6.26}$$

Fulfill the Laplace transformation. One has to chose for the zero moment of the time the moment which essentially precedes PIFD: $t_{max} \gg \Delta t$. The last equation will be transformed to

$$pv = 2y \frac{\partial v}{\partial y} + \frac{\partial^2 v}{\partial y^2} \quad . \tag{2.6.27}$$

To put the boundary condition one has to consider this equation on the boundary between the precritical and the critical regions. Then the second derivative $\frac{\partial^2 v}{\partial y^2}$ isn't essential and this equation will be reduced to

$$pv = 2y \frac{\partial v}{\partial y} \quad . \tag{2.6.28}$$

[21] The square approximation can be spread over the critical region.

Due to the homogeneous character of the last equation the function v can be determined only with the arbitrary factor $v_0(p)$ which is the function of p. The solution of the last equation with the natural physical boundary conditions can be easily found

$$v = v_0(p) \mid y \mid^{p/2} \exp(\frac{pc_1}{2}) \exp(c_2) \quad , \tag{2.6.29}$$

where c_1 and c_2 are the arbitrary constants.

The possibility of the translation over time and p allows to give the concrete calculation of v_0 only in the presence of c_1, c_2.

The determination of these constants by the integration over the region of the small sizes is impossible. Let us leave them as the unknown ones.

The function $v_0(p)$ is determined by the Laplace transformation of the boundary condition of the type $\sim \exp(-(\frac{t-t_{max}}{\Delta t})^2)$ from the precritical region

$$v_0(p) = const \int_0^\infty \exp(-pt) \exp(-(\frac{t - t_{max}}{\Delta t})^2) dt \quad . \tag{2.6.30}$$

After the integration on p from

$$t_{max} - (\Delta t)^2 \frac{p}{2} \gg \Delta t \quad , \tag{2.6.31}$$

one can come to

$$v_0(p) = const \pi^{1/2} \Delta t \exp(-pt_{max} + (\Delta t)^2 \frac{p^2}{4}) \quad . \tag{2.6.32}$$

The last inequality can be reduced to

$$t_{max} \gg (\Delta t)^2 \frac{p}{2} \quad . \tag{2.6.33}$$

The expression for $v_0(p)$ allows to come to the expression for v

$$v = const \pi^{1/2} \Delta t \exp(-pt_{max} + (\Delta t)^2 \frac{p^2}{4}) \mid y \mid^{p/2} \exp(pc_1/2) \exp(c_2) \quad . \tag{2.6.34}$$

Expression (2.6.32) is valid only at the lower boundary of the critical region but it will be used only as the boundary condition.

Now the evolution in the critical region will be considered. In the Fokker-Planck approximation one can write (2.6.26) or (2.6.27). The solution which is vanished at y has the form

$$v = \frac{1}{2} A_p i^{p/2} erfc(y) \quad , \tag{2.6.35}$$

where A_p is some constant independent on y and $i^n erfc(y)$ is the function which can be expressed through the function of parabolic cylinder $D_q(y)$ as

$$i^{p/2} erfc(y) = \exp(-y^2/2) D_{-\frac{p}{2}-1}(2^{1/2} y) \quad .$$

After taking into account the asymptote at big y

$$i^n erfc(y) = \frac{2 \mid y \mid^n}{\Gamma(n+1)} \tag{2.6.36}$$

and (2.6.29) one can get the expression for A_p

$$A_p = v_0(p) \exp(p\frac{c_1}{2}) \exp(c_2) \Gamma(\frac{p}{2}+1) \quad . \tag{2.6.37}$$

Then (2.6.35) transforms to

$$v = v_0(p) \exp(p\frac{c_1}{2}) \exp(c_2) \Gamma(\frac{p}{2}+1) i^{p/2} erfc(y)/2 \quad . \tag{2.6.38}$$

To get the rate of nucleation it is possible to fulfill the inverse Laplace transformation and to use the explicit formula. One can also use the asymptote v_{as} at $y \to \infty$ and then calculate the rate of nucleation.

The asymptote of the obtained solution is

$$i^n erfc(y) \to \exp(-y^2) \frac{2}{\pi^{1/2}} (2y)^{-n-1}, \quad y \to \infty \quad . \tag{2.6.39}$$

Then for v_{as} one can get the following expression

$$v_{as} = v_0(p) \exp(pc_1/2) \exp(c_2) \Gamma(\frac{p}{2}+1) \exp(-y^2) \frac{1}{\pi^{1/2}} (2y)^{-(p/2)-1} \quad . \tag{2.6.40}$$

Fulfill the inverse Laplace transformation

$$v_{as}(t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \exp(pt) v_{as}(p) dp \tag{2.6.41}$$

and get

$$v_{as}(t) = \frac{const \Delta t}{\pi} \exp(-y^2) \exp(c_2) \exp(-(\Delta t)^2 p_0^2) \int_{-\infty}^{\infty} \exp[-(p - ip_0)^2 \Delta t^2] \Gamma(ip+1) (2y)^{-ip-1} dp \quad , \tag{2.6.42}$$

where

$$p_0 = \frac{\frac{c_1}{2} - t_{max} + t}{(\Delta t)^2} \quad .$$

The integral in the last expression for $v_{as}(t)$ can be calculated by the steepens descent method. The leading term corresponds to the stationary approximation. Taking into account the first two terms of expansion one can get

$$v_{as}(t) = \frac{const}{\pi^{1/2}} \exp(-y^2) \exp(c_2) \exp(-(\Delta t)^2 p_0^2) \Gamma(-p_0+1)(2y)^{(p_0-1)} \tag{2.6.43}$$

$$[1 - (\Delta t)^{-2}[\frac{\psi^2(a) + \psi'(a)}{4} + \frac{\ln^2(2y)}{4} - \ln(2y)\frac{\psi(a)}{2}]] \quad ,$$

$$a = -p_0 + 1 \quad .$$

Calculate the rate of nucleation according to

$$j = -\exp(y^2)\frac{\partial}{\partial y} v_{as}(t) \quad . \tag{2.6.44}$$

Then having neglected the terms vanished at $y \to \infty$ one can get

$$j = \frac{const}{\pi^{1/2}} \exp(c_2) \exp(-(\Delta t)^2 p_0^2) \Gamma(-p_0+1)(2y)^{p_0} \tag{2.6.45}$$

$$[1 - (\Delta t)^{-2}[\frac{\psi^2(a) + \psi'(a)}{4} + \frac{\ln^2(2y)}{4} - \ln(2y)\frac{\psi(a)}{2}] + ...] \quad .$$

The experimentally observed value is the total number of droplets. It is proportional to

$$J = \int_{-\infty}^{\infty} j dt \quad . \tag{2.6.46}$$

After the end of PIFD in the square approximation one can see that the already formed droplets begin to disappear. It means that the boundary of the critical region begin to move along the axis of sizes. So, after $(2 \div 3)\Delta t$ one has to stabilize the level of the ideal supersaturation.

The trivial consideration leads to

$$J = \int_{-\infty}^{\infty} \frac{const}{\pi^{1/2}} \exp(c_2) \exp(-(\Delta t)^2 p_0^2) \Gamma(-p_0+1)(2y)^{p_0} \tag{2.6.47}$$

$$[1 - (\Delta t)^{-2}[\frac{\psi^2(a) + \psi'(a)}{4} + \frac{\ln^2(2y)}{4} - \ln(2y)\frac{\psi(a)}{2}] + ...] dt \quad .$$

The integral can be taken by the steepens descent method

$$J = \int_{-\infty}^{\infty} \frac{const\Delta t}{\pi^{1/2}} \exp(c_2) \exp(-z^2)\Gamma(1)$$
$$(1 - \frac{z}{\Delta t}\psi(1) + \frac{z^2}{2(\Delta t)^2}(\psi^2(1) + \psi'(1)) + ...)$$
$$(1 + \frac{z}{\Delta t}\ln(2y) + \frac{z^2}{(\Delta t)^2}\frac{\ln^2(2y)}{2} + ...) \tag{2.6.48}$$
$$(1 - (\Delta t)^{-2}(\frac{\psi^2(1) + \psi'(1)}{4} + \frac{\ln^2(2y)}{4} - \ln(2y)\frac{\psi(1)}{2}) + ...)dz \quad .$$

One can see that the coefficients in front of $(\Delta t)^0$, $(\Delta t)^{-1}$ go to zero. The same effect can be seen in the more high orders of $(\Delta t)^{-1}$.

Then

$$J = J_{st} \quad , \tag{2.6.49}$$

where J_{st} is the value of J calculated in the stationary approximation of the classical nucleation theory.

It is important to notice the absence of c_1 and c_2.

To generalize the analysis consider the variation of the supersaturation in the form of impulse. Then at the big values of y one can get

$$\begin{aligned} v_0(t) &= 0 \quad t < 0 \quad , \\ v_0(t) &= 1 \quad 0 < t > \Delta t \quad , \\ v_0(t) &= 0 \quad t > \Delta t \quad . \end{aligned} \tag{2.6.50}$$

After the Laplace transformation

$$v_0(p) = [1 - \exp(-p\Delta t)]/p \quad . \tag{2.6.51}$$

For the big positive values of y one can get

$$v_{as}(p) \sim [1 - \exp(-p\Delta t)] \exp(\frac{pc_1}{2}) \exp(c_2)$$
$$\Gamma(\frac{p}{2}) \exp(-y^2)(2y)^{-1-p/2} const \quad . \tag{2.6.52}$$

After the inverse Laplace transformation

$$v_{as}(t) = (2\pi i)^{-1} \int_{-i\infty}^{i\infty} [1 - \exp(-p\Delta t)] \exp(pc_1/2) \exp(c_2)$$

$$\Gamma(p/2)\exp(-y^2)(2y)^{-(p/2)-1}\exp(pt)dp\ const \quad , \tag{2.6.53}$$

the calculation of the flow j in the leading in y term can be reduced to the multiplication of v on $2y\exp(y^2)$. Then one can get

$$j = -(2\pi i)^{-1}\int_{-i\infty}^{i\infty}[1-\exp(-p\Delta t)]$$
$$\exp(pc_1/2)\exp(c_2)\Gamma(p/2)(2y)^{-p/2}\exp(pt)dp\ const \quad . \tag{2.6.54}$$

The flow can be written in the following form

$$J = -\int_0^\infty dt(2\pi i)^{-1}\int_{-i\infty}^{i\infty}[1-\exp(-p\Delta t)]$$
$$\exp(\frac{pc_1}{2})\exp(c_2)\Gamma(\frac{p}{2})(2y)^{-p/2}\exp(pt)dp\ const \quad . \tag{2.6.55}$$

The subintegral function has the pole at $p = 0$.

Decompose the subintegral function in the Loran seria. For the regular part it is possible to change the sequence of integration. Then

$$\int_0^\infty dt\exp(ipt) = \delta(p)/2 \quad . \tag{2.6.56}$$

One can see that δ-function requires to put $p = 0$ and the result doesn't depend on Δt.

For the singular part in the limit $p \to 0$ (with account $\Gamma(p/2)(2y)^{-p/2} \to \frac{2}{p}$) one can have

$$(2\pi i)^{-1}\int_{-i\infty}^{i\infty}\exp(p(t+\frac{c_1}{2}))(1-\exp(-p\Delta t))p^{-1}dp \quad . \tag{2.6.57}$$

The result is reduced to the inverse Laplace transformation which reconstructs v_0. But the simple translation[22] can not lead to the nonstationary effects.

Certainly, all considerations are made in the approximation of the stable boundaries of the critical region. But this approximation is rather precise.

[22]The argument will be $t + \frac{c_1}{2}$ instead of t.

Every functional dependence can be interpreted as the superposition of the already considered impulses. So this result has the general significance.

The kinetic equation has the divergent form. It can be seen that it is possible to integrate this equation on time and then integrate by parts.

2.7 Kinetics of the homogeneous and heterogeneous condensation

2.7.1 Effective ideal supersaturation

The following consideration is based on the inequality

$$I_s(\zeta) \gg \bar{I}_s(\zeta) \tag{2.7.1}$$

which is very strong. In the majority of the situations even the small number of the heterogeneous centers η_{tot} can not lead to the violation of the mentioned inequality.

The nontrivial situation occurs only when there is a small number of the heterogeneous centers and the supersaturation continues to grow. Then the intensity of the homogeneous rate of nucleation can become comparable to the heterogeneous rate at the moment of exhausting of the heterogeneous centers. So the number of the droplets formed on the heterogeneous centers is comparable with the number of the droplets formed homogeneously. But the droplets on the heterogeneous centers plays the important role in the formation of the external conditions for the heterogeneous nucleation. So, the nontrivial situation really takes place.

We shall consider the open system. The closed system is described analogously[23].

Consider the balance equation

$$\Phi = \zeta + g_{hom} + g_{het} \quad , \tag{2.7.2}$$

where g_{het} is the quantity of the substance in the droplets formed on the heterogeneous centers, g_{hom} is the quantity of the substance in the droplets formed homogeneously. The values g_{hom} and g_{het} are taken in the units of n_∞. The moment (and the values in this moment) from the intensive heterogeneous formation will be denoted by the upper index

[23]The estimates analogous to the further consideration will be even stronger.

"*". The moment (and the values in this moment) from the intensive homogeneous formation of the droplets will be denoted by the lower index "*".

As far as the homogeneous intensive formation of the droplets can occur only near Φ^* which are essentially greater than the supersaturation of the intensive heterogeneous formation then one can use the monodisperse approximation for the substance in the heterogeneously formed droplets. This leads to

$$\Phi = \zeta + \frac{\eta_{tot}}{n_\infty} y^3 + g_{hom} \quad , \tag{2.7.3}$$

where y is the current size of the droplets formed heterogeneously.

Introduce the "effective ideal supersaturation" $\tilde{\Phi}$ according to

$$\tilde{\Phi}(t) = \Phi(t) - \frac{\eta_{tot}}{n_\infty} y^3(t) \quad . \tag{2.7.4}$$

One can analytically show that ζ is close to $\tilde{\Phi}$ until the final of the period of intensive homogeneous nucleation (one can not calculate the size spectrum on the base of $\tilde{\Phi}$). The value of $\tilde{\Phi}(t)$ depends on the consumption of the vapor by the heterogeneously formed droplets. As far as $\tilde{\Phi}$ is close to ζ one can get the approximate equation

$$\tilde{\Phi} = \frac{dy}{dt}\tau \quad , \quad t \leq t_* \quad . \tag{2.7.5}$$

Then one can get the equation for y as the function[24] of time

$$\tau \frac{dy}{dt} = \Phi(t) - \frac{\eta_{tot}}{n_\infty} y(t)^3 \tag{2.7.6}$$

with the initial condition

$$y|_{t=t^*} = 0 \quad . \tag{2.7.7}$$

After the transition of the zero point to t^* assume Φ the linear function of time

$$\Phi = \Phi^* + At \tag{2.7.8}$$

Then one can get

$$\tau \frac{dy}{dt} = \Phi^* + At - y^3(t) \frac{\eta_{tot}}{n_\infty} \tag{2.7.9}$$

with the initial condition

$$y|_{t=0} = 0 \quad . \tag{2.7.10}$$

It is possible to take for $\tilde{\Phi}$ the second or the third iteration.

[24]The further construction will be valid even when Φ is the polynomial function.

2.7.2 The system of the condensation equations at the period of homogeneous nucleation

The value $\tilde{\Phi}$ allows to determine the main characteristics of the homogeneous condensation.

Introduce the coordinate z with the velocity

$$\frac{dz}{dt} = \frac{\zeta}{\tau} \quad . \tag{2.7.11}$$

Add the initial condition

$$z|_{t=t_*} = 0 \quad . \tag{2.7.12}$$

Introduce the variable

$$x = z - \rho \quad . \tag{2.7.13}$$

Denote via $f(x)$ the distribution over x (or z). This distribution is taken in the units of n_∞ and is considered in the unit volume.

As far as z and ρ have one and the same velocity then the every droplet has the constant value of x during the whole growth. The moment of the formation of the droplets with the given x can be denoted via $t(x)$. One can get the following expression for g_{hom}

$$g_{hom} = \int_{-\infty}^{z} (z-x)^3 f(x) dx \quad . \tag{2.7.14}$$

The balance equation can be written as

$$\tilde{\Phi}(z) = \zeta(z) + \int_{-\infty}^{z} (z-x)^3 f(x) dx \quad . \tag{2.7.15}$$

We have to make some approximations. Introduce the characteristic width ρ_p of the spectrum and the characteristic time of the variation of the supersaturation t_p. Suppose the validity of the following equation

$$\bar{t}_s \ll t_p \quad , \tag{2.7.16}$$

where $\bar{t}_s$ is the time of establishing of the stationary state in the region $\rho < (3 \div 5)\rho_c$. One can take for $\bar{t}_s$ the following estimate[25]

$$\bar{t}_s = \frac{4a\tau}{3\ln^2(\zeta+1)(\zeta+1)} \quad . \tag{2.7.17}$$

[25] The problem is to overcome the activation barrier but not to observe the stationary state at the boundary of the super critical region.

When (2.7.16) is valid during PIFD then one can assume that the state of the droplets with the size $\rho < (3 \div 5)\rho_c$ is the quasi stationary one. For the quasi stationary distribution $f_s(\zeta)$, in the units of n_∞ one can take the following expression

$$f_s(\zeta) = (\frac{a}{\pi})^{1/2} \frac{(\zeta+1)^2}{\zeta} \exp(-\bar{F}_{\nu_c}(\zeta)) \quad , \tag{2.7.18}$$

where $\bar{F}_{\nu_c} = \frac{a}{3}\rho_c^2$ is the free energy of the homogeneously formed embryo. The size of the critical embryo is defined by $\rho_c = \frac{2a}{3\ln(\zeta+1)}$.

One can use $f_s(\zeta)$ as the boundary condition for the distribution $f(x)$ from the small sizes. If

$$\rho_p \gg \rho_c \quad , \tag{2.7.19}$$

then the boundary condition in the expression for g_{hom} in (2.7.15) can be transformed to $\rho = 0$. One can spread the regular growth from $\rho \geq (3 \div 5)\rho_c$ to all sizes of the droplets and get the following equation

$$f(x) = f_s(\zeta(x)) \quad . \tag{2.7.20}$$

The following estimate

$$\frac{|\zeta_* - \tilde{\Phi}_*|}{\tilde{\Phi}_*} \leq \bar{\Gamma}^{-1} \quad , \tag{2.7.21}$$

where

$$\bar{\Gamma} = -\zeta \frac{d\bar{F}_{\nu_c}}{d\zeta}|_{\zeta=\Phi_*} \tag{2.7.22}$$

will be valid. The value of $\bar{\Gamma}$ is approximately equal to the number of the molecules in the critical embryo and the value of $\bar{\Gamma}$ is big. This allows to get for f_s the following approximation

$$f(x) = f_s(\tilde{\Phi}_*) \exp\{\frac{\bar{\Gamma}}{\tilde{\Phi}}(\zeta(x) - \tilde{\Phi}_*)\} \quad . \tag{2.7.23}$$

From the last equation it is clear that when ζ deviates from $\tilde{\Phi}_*$ by the small value $\bar{\Gamma}^{-1}$ then the height of the activation barrier changes in e times. So, the characteristic variation of the supersaturation at PIFD has the order of $\bar{\Gamma}^{-1}$.

To apply the method of the disbalanced iterations one has to show that the supersaturation can be linearized during the whole period of the homogeneous nucleation

$$\tilde{\Phi}(x) = \tilde{\Phi}_* + \frac{\tilde{\Phi}_*}{\bar{\Gamma}} cx \quad , \tag{2.7.24}$$

where

$$c = \frac{\bar{\Gamma}}{\tilde{\Phi}_*} \frac{d\tilde{\Phi}(x)}{dx}|_{x=0} \quad . \tag{2.7.25}$$

Let the maximum of ζ be attained at $d\tilde{\Phi}/dt = \mu d\Phi/dt$ where μ is the positive parameter. One can get

$$N_{hom} n_\infty \rho_p^2 = \frac{\mu}{1-\mu} \eta_{tot} y^2 \quad . \tag{2.7.26}$$

Estimate the influence of the homogeneously formed droplets and heterogeneously formed droplets on $d^2\zeta/dt^2$. The influence of the homogeneously formed droplets can be estimated by the value of the order $\rho_p N_{hom}(\zeta_*/\tau)^2$. The influence of the heterogeneously formed droplets can be estimated by the value of the order $(\eta_{tot}/n_\infty) y(\zeta_*/\tau)^2$. To linearize the effective supersaturation it is necessary to have

$$\rho_p N_{hom} n_\infty \gg y_* \eta_{tot} \quad . \tag{2.7.27}$$

Due to $\rho_p \ll y_*$ and (2.7.26) the required inequality is valid for all μ which aren't too small.

For very small μ due to the smallness of the relative deviation of $\tilde{\Phi}_m$ from Φ_m and the negative value of $d^2\tilde{\Phi}/dt^2$ one can see that the relative deviation of ζ_* from $\tilde{\Phi}_m$ is rather small.

According to the already established law of inertion of the characteristics of the nucleation one can take for the characteristic halfwidth of the spectrum the value of ρ_0 of the characteristic width under the simultaneous creation of the initial supersaturation

$$\rho_0 \simeq [\frac{\zeta_*}{\bar{\Gamma} f_s(\zeta_*)}]^{1/4} \quad . \tag{2.7.28}$$

Determine the imaginary width of the spectrum ρ_i by the homogeneously formed droplets. Having differentiated the balance equation two times one can get for the second derivative of $\tilde{\Phi}$ in the point of the maximum of $\tilde{\Phi}$ the following expression

$$\frac{d^2\tilde{\Phi}}{dt^2}|_{t=t_m} = -2\sqrt{3} \frac{\eta_{tot}^{1/2} A^{1/2} \tilde{\Phi}_m^{3/2}}{n_\infty^{1/2} \tau^{3/2}} \quad . \tag{2.7.29}$$

The value of y_m satisfies to the inequality

$$y_m = (\frac{A\tau n_\infty}{3\eta_{tot}\tilde{\Phi}_m})^{1/2} \quad . \tag{2.7.30}$$

Under the restriction of the second derivative one can get for the characteristic halfwidth of the spectrum

$$\rho_i = [\frac{1}{2}\frac{\bar{\Gamma}}{\zeta_*}(-\frac{d^2\zeta}{dt^2})(\frac{\tau}{\zeta_*})^2]^{-1/2} \quad , \tag{2.7.31}$$

where the approximation (2.7.23) for $f(x)$ is taken into account and the derivative is taken in the point of the maximum of the supersaturation. As far as we consider the halfwidth without the vapor consumption by the homogeneously formed droplets it is necessary to substitute instead of $d^2\zeta/dt^2$ the value of $d^2\tilde{\Phi}/dt^2|_{t=t_m}$. Then

$$\rho_i^4 \simeq \frac{\tilde{\Phi}_*^3 n_\infty}{\bar{\Gamma}^2 \eta_{tot} A\tau} \quad . \tag{2.7.32}$$

Determine the ratio ρ_0/ρ_i. According to the last equation and to (2.7.28) one can get

$$\frac{\rho_0}{\rho_i} = (\frac{\bar{\Gamma}\eta_{tot}A\tau}{\tilde{\Phi}_*^2 n_\infty f_s(\tilde{\Phi}_*)})^{1/4} \equiv q(\tilde{\Phi}_*) \quad . \tag{2.7.33}$$

The values of $q(\tilde{\Phi}_*)$ and $f_s(\tilde{\Phi}_*)$ are the sharp functions of $\tilde{\Phi}_*$. When $q \ll 1$ the linearization of $\tilde{\Phi}$ at the period of nucleation is valid. The case $q \ll 1$ is case of the moderate influence of the heterogeneously formed droplets on the process of the homogeneous condensation. The case $q \gg 1$ is the case of the strong influence of the heterogeneously formed droplets on the process of the homogeneous condensation. Here we shall consider the cases $q \ll 1$ and $q \gg 1$. As far as q grows rapidly when $\tilde{\Phi}_*$ grows these cases practically cover all $\tilde{\Phi}_*$. The generalization for the intermediate situation will be given in the chapter four.

2.7.3 The case of the moderate influence of the heterogeneously formed droplets

Linearize $\tilde{\Phi}(x)$ according to (2.7.24), (2.7.25). Then the equation for g_{hom} with the account of (2.7.23) and the account of the balance equation can be written in the following form

$$g_{hom}(z) = f_s(\tilde{\Phi}_*)\int_{-\infty}^{z}(z-x)^3\exp(cx - \frac{\bar{\Gamma}}{\tilde{\Phi}_*}g_{hom}(x))dx \quad . \tag{2.7.34}$$

The value of $f_s(\tilde{\Phi}_*)$ in the last equation is some parameter. It will be calculated from the condition for t_* after the form of the size spectrum

is found. Due to the choice of t_*

$$\bar{N}(0) = \frac{\bar{N}(\infty)}{2} \quad , \tag{2.7.35}$$

where $\bar{N}(x)n_\infty$ is the number of the droplets formed homogeneously until the moment $t(x)$. So, $\bar{N}(0)n_\infty$ is the number of the droplets at t_*. The value of $\bar{N}(x)$ can be found as

$$\bar{N}(z) = f_s(\tilde{\Phi}_*) \int_{-\infty}^{z} \exp(cx - \frac{\bar{\Gamma}}{\tilde{\Phi}_*} g_{hom}(x))dx \quad . \tag{2.7.36}$$

The spectrum is given by

$$f(x) = f_s(\tilde{\Phi}_*) \exp(cx - \frac{\bar{\Gamma}}{\tilde{\Phi}_*} g_{hom}(x)) \quad . \tag{2.7.37}$$

Construct the iterations for g_{hom}, $\bar{N}(z)$, $f(x)$

$$g_{i+1\ hom}(z) = f_s(\tilde{\Phi}_*) \int_{-\infty}^{z} (z-x)^3 \exp(cx - \frac{\bar{\Gamma}}{\tilde{\Phi}_*} g_{i\ hom}(x))dx \quad , \tag{2.7.38}$$

$$\bar{N}_{i+1}(z) = f_s(\tilde{\Phi}_*) \int_{-\infty}^{z} \exp(cx - \frac{\bar{\Gamma}}{\tilde{\Phi}_*} g_{i\ hom}(x))dx \quad , \tag{2.7.39}$$

$$f_{i+1}(x) = f_s(\tilde{\Phi}_*) \exp(cx - \frac{\bar{\Gamma}}{\tilde{\Phi}_*} g_{i\ hom}(x)) \quad . \tag{2.7.40}$$

The initial approximation will be $g_{0\ hom} = 0$. Then $g_{0\ hom} < g_{hom}$. The r.h.s. of (2.7.38) is positive, then $g_{i\ hom} > g_{0\ hom}$ and particularly $g_{2\ hom} > g_{0\ hom}$. So, under the unique choice of t_* (and of the variables z, x) one can get the following chains of inequalities

$$g_{0\ hom} < ... < g_{2i\ hom} < ... < g_{hom} < ... < g_{2i+1\ hom} < ... < g_{1\ hom}, \tag{2.7.41}$$

$$\bar{N}_2 < \bar{N}_4 < ... < \bar{N}_{2i} < ... < \bar{N} < ... < \bar{N}_{2i+1} < ... < \bar{N}_3 < \bar{N}_1, \tag{2.7.42}$$

$$f_2 < f_4 < ... < f_{2i} < ... < f < ... < f_{2i+1} < ... < f_3 < f_1, \tag{2.7.43}$$

which allow to estimate the accuracy of the approximations. The main characteristic is the number of the droplets. One can get

$$|\bar{N}(\infty) - \bar{N}_i(\infty)| < |\bar{N}_{i+1}(\infty) - \bar{N}_i(\infty)| \tag{2.7.44}$$

for the accuracy of the iterations.

Calculate the iterations. In the first approximation

$$g_{1\ hom}(z) = \frac{6f_s(\tilde{\Phi}_*)\exp(cz)}{c^4} \quad , \tag{2.7.45}$$

$$\bar{N}_1(z) = \frac{f_s(\tilde{\Phi}_*)\exp(cz)}{c} \quad , \tag{2.7.46}$$

$$f_1(x) = f_s(\tilde{\Phi}_*)\exp(cx) \quad . \tag{2.7.47}$$

In the second approximation

$$g_{2\ hom}(z) = f_s(\tilde{\Phi}_*)\int_{-\infty}^{z}(z-x)^3\exp(cx - \frac{6\bar{\Gamma}f_s(\tilde{\Phi}_*)}{\tilde{\Phi}_* c^4}\exp(cx))dx \quad , \tag{2.7.48}$$

$$\bar{N}_2(z) = f_s(\tilde{\Phi}_*)\int_{-\infty}^{z}\exp(cx - \frac{6\bar{\Gamma}f_s(\tilde{\Phi}_*)}{\tilde{\Phi}_* c^4}\exp(cx))dx \quad , \tag{2.7.49}$$

$$f_2(x) = f_s(\tilde{\Phi}_*)\exp(cx - \frac{6\bar{\Gamma}f_s(\tilde{\Phi}_*)}{\tilde{\Phi}_* c^4}\exp(cx)) \quad . \tag{2.7.50}$$

After the calculation of the integral

$$\bar{N}_2(z) = \frac{c^3\tilde{\Phi}_*}{6\bar{\Gamma}}[1 - \exp(-\frac{6\Gamma f_s(\tilde{\Phi}_*)}{\tilde{\Phi}_* c^4}\exp(cz))] \quad . \tag{2.7.51}$$

Calculate $\bar{N}(z)$ in the third approximation

$$\bar{N}_3(z) = f_s(\tilde{\Phi}_*)\int_{-\infty}^{z}dx\exp(cx - \frac{\bar{\Gamma}}{\tilde{\Phi}_*}f_s(\tilde{\Phi}_*)\int_{-\infty}^{x}dx' \\ (x-x')^3\exp(cx' - \frac{6\bar{\Gamma}f_s(\tilde{\Phi}_*)}{\tilde{\Phi}_* c^4}\exp(cx'))) \quad . \tag{2.7.52}$$

One can show

$$\frac{|\bar{N}_2(\infty) - \bar{N}_3(\infty)|}{\bar{N}_2(\infty)} = 0.15 \quad . \tag{2.7.53}$$

So, at the period of the homogeneous nucleation

$$g_{hom} \simeq g_{1\ hom} \ , \quad \bar{N} \simeq \bar{N}_2 \ , \quad f(x) \simeq f_2(x) \quad . \tag{2.7.54}$$

Consider the expression for g_{hom}. After the final of the period of the homogeneous nucleation one can put the upper limit of integration to ∞:

$$g_{hom}(z) \to \int_{-\infty}^{\infty} (z-x)^3 f(x) dx \quad , \tag{2.7.55}$$

which allow to present g_{hom} as

$$g_{hom}(z) \to \hat{g}_{3\ hom} + z\hat{g}_{2\ hom} + z^2\hat{g}_{1\ hom} + z^3\hat{g}_{0\ hom} \quad , \tag{2.7.56}$$

where $\hat{g}_{0\ hom}$, $\hat{g}_{1\ hom}$, $\hat{g}_{2\ hom}$, $\hat{g}_{3\ hom}$ are defined according to

$$\hat{g}_{0\ hom} = \int_{-\infty}^{\infty} f(x) dx = \bar{N}(\infty) n_{\infty} \quad , \tag{2.7.57}$$

$$\hat{g}_{1\ hom} = -3 \int_{-\infty}^{\infty} x f(x) dx \quad , \tag{2.7.58}$$

$$\hat{g}_{2\ hom} = 3 \int_{-\infty}^{\infty} x^2 f(x) dx \quad , \tag{2.7.59}$$

$$\hat{g}_{3\ hom} = - \int_{-\infty}^{\infty} x^3 f(x) dx \quad . \tag{2.7.60}$$

Coefficients $\hat{g}_{i\ hom}$ don't depend on z. After the substitution of (2.7.56) into the balance equation one can see that the evolution is determined by some first momentums of $f(x)$. It will be until the coalescence.

For $\hat{g}_{i\ hom}$ in the second approximation one can get

$$\hat{g}_{0\ hom} = f_s(\tilde{\Phi}_*) \int_{-\infty}^{\infty} dx \exp(cx - \frac{6\bar{\Gamma} f_s(\tilde{\Phi}_*)}{\tilde{\Phi}_* c^4} \exp(cx)) \quad , \tag{2.7.61}$$

$$\hat{g}_{1\ hom} = -3 f_s(\tilde{\Phi}_*) \int_{-\infty}^{\infty} dx x \exp(cx - \frac{6\bar{\Gamma} f_s(\tilde{\Phi}_*)}{\tilde{\Phi}_* c^4} \exp(cx)) \quad , \tag{2.7.62}$$

$$\hat{g}_{2\ hom} = 3 f_s(\tilde{\Phi}_*) \int_{-\infty}^{\infty} dx x^2 \exp(cx - \frac{6\bar{\Gamma} f_s(\tilde{\Phi}_*)}{\tilde{\Phi}_* c^4} \exp(cx)) \quad , \tag{2.7.63}$$

$$\hat{g}_{3\ hom} = - f_s(\tilde{\Phi}_*) \int_{-\infty}^{\infty} dx x^3 \exp(cx - \frac{6\bar{\Gamma} f_s(\tilde{\Phi}_*)}{\tilde{\Phi}_* c^4} \exp(cx)) \quad . \tag{2.7.64}$$

Introduce the variable

$$\xi = cx + L \ , \quad L = \ln \frac{6\bar{\Gamma} f_s(\tilde{\Phi}_*)}{\tilde{\Phi}_* c^4} \quad . \tag{2.7.65}$$

Then (2.7.61) - (2.7.64) can be presented as

$$\hat{g}_{0\ hom} = \frac{\tilde{\Phi}_* a^3}{6\bar{\Gamma}} b_0 \quad , \tag{2.7.66}$$

$$\hat{g}_{1\ hom} = -\frac{\tilde{\Phi}_* a^2}{2\bar{\Gamma}} (b_1 - L b_0) \quad , \tag{2.7.67}$$

$$\hat{g}_{2\ hom} = \frac{\tilde{\Phi}_* a}{2\bar{\Gamma}} (b_2 - 2L b_1 + L^2 b_0) \quad , \tag{2.7.68}$$

$$\hat{g}_{3\ hom} = -\frac{\tilde{\Phi}_*}{6\bar{\Gamma}} (b_3 - 3L b_2 + 3L^2 b_1 - L^3 b_0) \quad , \tag{2.7.69}$$

where

$$b_i = \int_{-\infty}^{\infty} \xi^i \exp(\xi - \exp(\xi)) d\xi \quad , \quad i = 0, 1, 2, 3$$

are some universal constants.

Due to $\bar{N} \simeq \bar{N}_2$, one can write the definition (2.7.35) of t_* as

$$6 f_s(\tilde{\Phi}_*) \bar{\Gamma} = \tilde{\Phi}_* c^4 \ln 2 \quad . \tag{2.7.70}$$

It can be solved analogously to the heterogeneous case.

Then one can come to

$$\hat{g}_{0\ hom} = \frac{\tilde{\Phi}_* a^3}{6\bar{\Gamma}} \quad , \tag{2.7.71}$$

$$\hat{g}_{1\ hom} = -0.1053 \frac{\tilde{\Phi}_* a^2}{\bar{\Gamma}} \quad , \tag{2.7.72}$$

$$\hat{g}_{2\ hom} = 0.8446 \frac{\tilde{\Phi}_* a}{\bar{\Gamma}} \quad , \tag{2.7.73}$$

$$\hat{g}_{3\ hom} = -0.5775 \frac{\tilde{\Phi}_*}{\bar{\Gamma}} \quad . \tag{2.7.74}$$

For the total number of the homogeneously formed droplets one can get

$$\bar{N}(\infty) = \frac{\tau^3 A^3 \bar{\Gamma}^2}{6 \tilde{\Phi}_*^5} \quad . \tag{2.7.75}$$

One can define the right halfwidth $\bar{\Delta}_+ x$ and the left halfwidth $\bar{\Delta}_- x$ by

$$|\bar{N}(0) - \bar{N}(\mp \bar{\Delta}_{\mp} x)| = |\bar{N}(0) - \bar{N}(\mp\infty)|(1 - \delta) \quad , \tag{2.7.76}$$

where δ is some parameter. Outside the interval $[-\bar{\Delta}_- x, \bar{\Delta}_+ x]$ the relative number of the droplets will be δ. The value of δ can be chosen as the error of the second iteration. For $\bar{\Delta}_\mp x$ one can get the following equations

$$\bar{\Delta}_+ x = \frac{1}{c} \ln \frac{\ln \frac{\delta}{2}}{\ln \frac{1}{2}} \quad , \tag{2.7.77}$$

$$\bar{\Delta}_- x = \frac{1}{c} \ln \frac{\ln \frac{1}{2}}{\ln(1 - \frac{\delta}{2})} \quad . \tag{2.7.78}$$

The moments t_{st} and t_{fin} corresponding to $x = -\bar{\Delta}_- x$ and $x = \bar{\Delta}_+ x$ can be considered as the start and the final of the period of the nucleation. They can be given by

$$\begin{aligned} t_{st} &= t_*(1 - \frac{1}{\bar{\Gamma}} c \bar{\Delta}_- x) \quad , \\ t_{fin} &= t_*(1 + \frac{1}{\bar{\Gamma}} c \bar{\Delta}_+ x) \quad . \end{aligned} \tag{2.7.79}$$

Universal solution

The balance equation can be written as

$$\tilde{\Phi}(z) = \zeta(z) + f_s(\tilde{\Phi}_*) \int_{-\infty}^{z} (z - x)^3 \exp(\frac{\bar{\Gamma}}{\tilde{\Phi}_*}(\zeta(x) - \tilde{\Phi}_*)) dx \quad , \tag{2.7.80}$$

for the unknown function $\zeta(x)$. After the differentiation on z one can get

$$\frac{d\tilde{\Phi}(z)}{dz} = \frac{d\zeta(z)}{dz} + 3 f_s(\tilde{\Phi}_*) \int_{-\infty}^{z} (z-x)^2 \exp(\frac{\bar{\Gamma}}{\tilde{\Phi}_*}(\zeta(x) - \tilde{\Phi}_*)) dx \quad . \tag{2.7.81}$$

Choose t_* as

$$\frac{d\tilde{\Phi}(z)}{dz}|_{z=0} = k^{-1} \frac{d\zeta(z)}{dz}|_{z=0} \quad , \tag{2.7.82}$$

where the parameter k is less than unity. The choice $k = 0$ corresponds to the choice of t_* as the moment of the maximum intensity of formation. Then one can get

$$\frac{\tilde{\Phi}(z)}{dz}|_{z-0} = \frac{3 f_s(\tilde{\Phi}_*)}{1 - k} \int_{-\infty}^{0} x^2 \exp(\frac{\bar{\Gamma}}{\tilde{\Phi}_*}(\zeta(x) - \tilde{\Phi}_*)) dx \quad . \tag{2.7.83}$$

Having linearized $\tilde{\Phi}$ in (2.7.80) one can see that

$$\tilde{\Phi}_* + z\frac{3f_s(\tilde{\Phi}_*)}{1-k}\int_{-\infty}^{0} x^2\exp(\frac{\bar{\Gamma}}{\tilde{\Phi}_*}(\zeta(x)-\tilde{\Phi}_*))dx = \\ \zeta(z) + f_s(\tilde{\Phi}_*)\int_{-\infty}^{z}(z-x)^3\exp(\frac{\bar{\Gamma}}{\tilde{\Phi}_*}(\zeta(x)-\tilde{\Phi}_*))dx \quad . \tag{2.7.84}$$

Transform x into $\rho_h x$ and z into $\rho_h z$, where ρ_h satisfies the condition

$$\rho_h^4 f_s(\tilde{\Phi}_*) = \frac{\tilde{\Phi}_*}{\bar{\Gamma}} \tag{2.7.85}$$

Then

$$z\frac{3}{1-k}\int_{-\infty}^{0} x^2\exp(\frac{\bar{\Gamma}}{\tilde{\Phi}_*}(\zeta(x)-\tilde{\Phi}_*))dx = \\ \frac{\bar{\Gamma}}{\tilde{\Phi}_*}(\zeta(x)-\tilde{\Phi}_*) + \int_{-\infty}^{z}(z-x)^3\exp(\frac{\bar{\Gamma}}{\tilde{\Phi}_*}(\zeta(x)-\tilde{\Phi}_*))dx \quad . \tag{2.7.86}$$

Introduce the function

$$\delta = \frac{\bar{\Gamma}}{\tilde{\Phi}_*}(\zeta(x)-\tilde{\Phi}_*) \tag{2.7.87}$$

and get the equation on δ

$$z\frac{3}{1-k}\int_{-\infty}^{0} x^2\exp(\delta(x))dx = \delta(z)+\int_{-\infty}^{z}(z-x)^3\exp(\delta(x))dx \ . \tag{2.7.88}$$

There are no parameters in the last equation. Then the function δ doesn't depend on the parameters of the problem. With some constant instead of the l.h.s. of the last equation one can come to the equation with the unique solution. It is necessary to choose this number to satisfy the condition for t_*. The values $\hat{g}_{i\ hom}$ can be presented in the form

$$\hat{g}_{i\ hom} = \frac{\tilde{\Phi}_* c^{3-i}}{\bar{\Gamma}}\hat{c}_i \quad , \tag{2.7.89}$$

where $\hat{c}_i$ are the constants which are universal for all initial conditions.

The equation on the parameters of the process can be written as

$$\frac{\bar{\Gamma} f_s(\tilde{\Phi}_*)}{\tilde{\Phi}_* c^4} = const \quad , \tag{2.7.90}$$

where the r.h.s. is constant for all external conditions.

One can write the universal equation in a slightly different form. Denote the point of the maximum of the supersaturation as z_m. The point $z = 0$ has the previous sense as the basic point in the approximations (2.7.23), (2.7.24).

Then (2.7.48) can be written in the following form

$$3\int_{-\infty}^{z_m}(z_m - x)^2 \exp(\delta(x))dxz = \delta(z) + \int_{-\infty}^{z}(z-x)^3 \exp(\delta(x))dx \quad . \tag{2.7.91}$$

All these constructions can be written for the arbitrary k.

From the last equation it follows that

$$3\int_{-\infty}^{z_m}(z_m - x)^2 \exp(\delta(x))dx = \frac{d\delta(z)}{dz} + 3\int_{-\infty}^{z}(z-x)^2 \exp(\delta(x))dx \quad . \tag{2.7.92}$$

One can come for the maximum of δ to the following expression

$$\delta(z_m) = 3\int_{-\infty}^{z_m}(z_m - x)^2 \exp(\delta(x))dxz_m - \int_{-\infty}^{z_m}(z_m-x)^3 \exp(\delta(x))dx \quad . \tag{2.7.93}$$

Having differentiated the last equation on z_m one can get

$$\frac{d\delta(z_m)}{dz_m} = 6\int_{-\infty}^{z_m}(z_m - x)\exp(\delta(x))dxz_m > 0 \quad . \tag{2.7.94}$$

The last inequality shows that when z_m grows then δ grows also.

Introduce the family $\delta_A(x)$ of the functions satisfying the equation

$$Az = \delta(z) + \int_{-\infty}^{z}(z-x)^3 \exp(\delta(x))dx \quad . \tag{2.7.95}$$

The solutions of (2.7.88) and (2.7.91) are from the family $\delta_A(x)$. The solutions of (2.7.91) and of the last equation coincides when

$$A = 3\int_{-\infty}^{z_m}(z_m - x)^2 \exp(\delta(x))dx \quad . \tag{2.7.96}$$

Having differentiated the last equation on z_m one can see that

$$\frac{dA}{dz_m} = 6\int_{-\infty}^{z_m}(z_m - x)\exp(\delta(x))dx > 0 \qquad (2.7.97)$$

Then one solution of (2.7.95) corresponds to one z_m and to one solution of (2.7.91).

The existence and the uniqueness of the solutions of all mentioned equations can be shown analogously to the heterogeneous case.

Represent the solution of (2.7.95) as the limit of solutions of equations

$$Az = \delta(z) + \int_{-a}^{z}(z - x)^3\exp(\delta(x))dx \qquad (2.7.98)$$

when $a \to \infty$. Having differentiated the last equation four times one can get

$$\frac{d^4\delta}{dz^4} = -6\exp(\delta(z)) \quad . \qquad (2.7.99)$$

The differential equations (2.7.91), (2.7.95) can be reduced to the same equation. For the equation which is obtained by the differentiating of (2.7.98) the initial conditions will be the following

$$\delta(-a) = -Aa \ , \ \delta'(-a) = A \ , \ \delta''(-a) = 0 \ , \ \delta'''(-a) = 0 \qquad (2.7.100)$$

Then from the uniqueness of the solution of the Caushi problem the equation (2.7.98) has one solution. Having used the iteration method one can estimate the difference between the solution of (2.7.95) and the solution (2.7.98). After the necessary estimates for the asymptotes of the solution one can put $a \to \infty$ and get that the equation (2.7.95) has no more than one solution. Then (2.7.85) and (2.7.91) have no more than one solution.

The situation when few solutions of (2.7.91) have one and the same maximum which is attained according to (2.7.94) at one and the same z_m can not take place. To show it one can substitute in (2.7.91) the lower limit of the integration by $-a$ then to take into account according to (2.7.97) that the l.h.s. when $-\infty$ is changed to $-a$ can not be changed and finally get that this equation has the unique solution. Then with the help of the estimates for δ at $x \to -\infty$ it is possible to put $a \to \infty$ and to get the uniqueness of the solution.

The uniqueness of the solution of (2.7.91) has the principal significance as far as in the transformation to (2.7.91) some new additional

solutions can appear. These solutions can lead to the new symmetry of the equation and as the consequence to the disappearing of the constants which extract the real solution.

The universality of δ and $\hat{c}_i$ allows to describe all processes of the condensation after the unique computer simulation of the process.

The results at $A = 14.8$ (it corresponds to maximum near $z = 0$) are the following

$$\hat{c}_0 = 0.184 \ , \ \hat{c}_1 = -1.095 \ , \ \hat{c}_2 = 0.288 \ , \ \hat{c}_3 = -0.962 \ \ .$$

Under the simultaneous creation of the supersaturation (the situation of decay) one can also use such approach. For the balance equation one can have

$$\zeta_0 = \zeta(z) + f_s(\zeta_0) \int_0^z (z-x)^3 \exp(\frac{\bar{\Gamma}}{\zeta_0}(\zeta(x) - \zeta_0))dx \ \ , \qquad (2.7.101)$$

where ζ_0 is the value of the initial supersaturation which is known. After the transformation from x to $\tilde{\rho}_h x$ and from z to $\tilde{\rho_h} z$ where

$$\tilde{\rho}_h = [\frac{\zeta_0}{\bar{\Gamma}(\zeta_0) f_s(\zeta_0)}]^{1/4} \ \ , \qquad (2.7.102)$$

one can get

$$-\frac{\bar{\Gamma}}{\zeta_0}(\zeta(x) - \zeta_0) = \int_0^z (z-x)^3 \exp(\frac{\bar{\Gamma}}{\zeta_0}(\zeta(x) - \zeta_0))dx \ \ . \qquad (2.7.103)$$

From the last equation it follows that $\bar{\Gamma}(\zeta(x) - \zeta_0)/\zeta_0$ doesn't depend on parameters. As far as the representation (2.7.56) is valid after the homogeneous nucleation one can use the mentioned approach. The existence and the uniqueness of the solution is evident as far as one can differentiate the balance equation four times and get the Caushi problem for differential equation of the forth order.

The main errors are connected with the linearization of $\tilde{\Phi}(x)$ and with the exponent approximation for $f(x)$. One can use the perturbation theory. The coefficients of the perturbation series will be presented through the values of the characteristics at t_* multiplied on the mean values on the distribution $\exp(\delta(x))$ from the products of x, $\delta(x)$, $\int_{-\infty}^{x} \delta(x')dx'$. So, the perturbation theory can be constructed after the unique computer simulation.

2.7.4 The case of the strong influence of the heterogeneously formed droplets.

The characteristic moment t_* can be taken as the moment of the maximum $\zeta(t)$.

The spectrum of the droplets can be found as

$$f(x) = f_s(\tilde{\Phi}(x)) \tag{2.7.104}$$

and with the help of (2.7.23) can be rewritten in the following form

$$f(x) = f_s(\tilde{\Phi}_m) \exp(\frac{\bar{\Gamma}}{\tilde{\Phi}_m}(\tilde{\Phi} - \tilde{\Phi}_m)) \quad . \tag{2.7.105}$$

On the base of $f(z)$ one can determine $g_{hom}(z)$ and $\bar{N}(z)$

$$\bar{N}(z) = f_s(\tilde{\Phi}_m) \int_{-\infty}^{z} \exp(\frac{\bar{\Gamma}}{\tilde{\Phi}_m}(\tilde{\Phi} - \tilde{\Phi}_m))dx \quad , \tag{2.7.106}$$

$$g_{hom}(z) = f_s(\tilde{\Phi}_m) \int_{-\infty}^{z} (z-x)^3 \exp(\frac{\bar{\Gamma}}{\tilde{\Phi}_m}(\tilde{\Phi}(x) - \tilde{\Phi}_m))dx \quad . \tag{2.7.107}$$

One has to know the approximation for $\tilde{\Phi}$ which guarantees the determination of $f_s(\tilde{\Phi}_m)$ with the high precision.

With the help of z, x one can find the approximation for $(\tilde{\Phi}(x) - \tilde{\Phi}_m)/\tilde{\Phi}_m$. Consider the equation for $\tilde{\Phi}(x)$ and differentiate it in time

$$A = \frac{d\tilde{\Phi}(t)}{dt} + 3\frac{\eta_{tot}}{n_\infty} y^2 \frac{\tilde{\Phi}(t)}{\tau} \quad . \tag{2.7.108}$$

Note that

$$z = y - y(t_m) \quad , \tag{2.7.109}$$

and one can come to

$$\frac{d\tilde{\Phi}(t)}{dt} = -3\frac{\eta_{tot}}{n_\infty} \frac{\tilde{\Phi}(t)}{\tau} [z^2 + 2zy(t_m)] \tag{2.7.110}$$

($z \ll y$ was taken into account).

As far as the supersaturation during the period of the nucleation has the variations of the order $\bar{\Gamma}^{-1}$ one can see that

$$d\tilde{\Phi}(t)/dt = (\tilde{\Phi}_m/\tau)(d\tilde{\Phi}/dz) \quad .$$

Having differentiated the mentioned equation one can get

$$\tilde{\Phi}(z) = -\frac{\eta_{tot}}{n_\infty}[z^3 + 3z^2 y(t_m)] + const \quad . \tag{2.7.111}$$

One can determine the value of *const* in the last equation from $\tilde{\Phi}(z)|_{z=0} = \tilde{\Phi}_m$. Then it is possible to get

$$\tilde{\Phi}(z) - \tilde{\Phi}_m = -\frac{\eta_{tot}}{n_\infty}[z^3 + 3z^2 y(t_m)] \quad . \tag{2.7.112}$$

The form of the spectrum can be found as

$$f(x) = f_s(\tilde{\Phi}_m) \exp(-\frac{\bar{\Gamma}\eta_{tot}}{\tilde{\Phi}_m n_\infty}(z^3 + 3y_m z^2)) \quad . \tag{2.7.113}$$

The right halfwidth of the spectrum $\bar{\Delta}_+ x$ and the left halfwidth of the spectrum $\bar{\Delta}_- x$ can be found from

$$\begin{aligned} 1 &= \frac{\bar{\Gamma}\eta_{tot}}{\tilde{\Phi}_* n_\infty}[(\bar{\Delta}_+ x)^3 + 3(\bar{\Delta}_+ x)^2 y_m] \quad , \\ 1 &= \frac{\bar{\Gamma}\eta_{tot}}{\tilde{\Phi}_* n_\infty}[-(\bar{\Delta}_- x)^3 + 3(\bar{\Delta}_- x)^2 y_m] \quad . \end{aligned} \tag{2.7.114}$$

Note the evident inequality

$$y_m \gg \bar{\Delta}_\pm x \tag{2.7.115}$$

at the period of homogeneous nucleation when z goes from $-\bar{\Delta}_- x$ to $\bar{\Delta}_+ x$. The first term in the r.h.s. of (2.7.112) can be neglected. Then

$$f(x) = f_s(\tilde{\Phi}_m) \exp(-3y_m \frac{\bar{\Gamma}\eta_{tot}}{\tilde{\Phi}_m n_\infty} z^2) \quad . \tag{2.7.116}$$

The total number of the droplets can be found as

$$\bar{N} = \sqrt{\pi} f_s(\tilde{\Phi}_m) z_h \quad , \tag{2.7.117}$$

where z_h is the halfwidth of the spectrum determined by

$$z_h = [\frac{\tilde{\Phi}_m n_\infty}{3\bar{\Gamma}\eta_{tot} y_m}]^{1/2} \quad . \tag{2.7.118}$$

All the coefficients $\hat{g}_{i\ hom}$, can be calculated in this approximation

$$\hat{g}_{0\ hom} = \bar{N} \quad , \tag{2.7.119}$$

$$\hat{g}_{1\ hom} = 0 \quad , \tag{2.7.120}$$

$$\hat{g}_{2\ hom} = \frac{3\sqrt{\pi}}{2} z_h^3 f_s(\tilde{\Phi}_m) \quad , \tag{2.7.121}$$

$$\hat{g}_{3\ hom} = 0 \quad . \tag{2.7.122}$$

2.7.5 Analysis of the approximations

For $\bar{\Gamma}$ the following estimate

$$40 \div 50 \leq \bar{\Gamma} \leq 10^2 \tag{2.7.123}$$

is valid. So, the third iteration for $\tilde{\Phi}_m$ is sufficient.

Consider the equation on the parameters of the process under the moderate influence of the heterogeneous centers. With the help of the definition of $\tilde{\Psi}$ taking into account $dx/dt = \zeta/\tau \approx \tilde{\Phi}_*/\tau$ one can come to

$$f_s(\tilde{\Phi}_*) = \frac{\tau^4 \tilde{\Psi}_*^4 \bar{\Gamma}^3 \ln 2}{6\tilde{\Phi}_*^7} \quad . \tag{2.7.124}$$

It is necessary to know $\tilde{\Psi}$ as the function of $\tilde{\Phi}$. In the iteration approximation one can get

$$\tilde{\Psi}_i(\tilde{\Phi}_i) = \tilde{\Psi}_i(t_i(\tilde{\Phi}_i)) \quad , \tag{2.7.125}$$

where $t_i(\tilde{\Phi})$ is the function inverse to $\tilde{\Phi}_i(t)$. According to the estimates for $\tilde{\Psi}$

$$\tilde{\Psi}_{2i+1}(t_{2i+1}(\tilde{\Phi})) > \tilde{\Psi}(\tilde{\Phi}) > \tilde{\Psi}_{2i}(t_{2i}(\tilde{\Phi})) \quad . \tag{2.7.126}$$

The function $6 f_s(\tilde{\Phi})\tilde{\Phi}_*^7/\bar{\Gamma}^3\tau^4 \ln 2$ is the sharp function of the supersaturation. Then the root of (2.7.124) is the unique one. One can have the following chain

$$\Phi_{*\ 2} < ... < \Phi_{*\ 2i} < ... < \Phi_* < ... < \Phi_{*\ 2i+1} < ... < \Phi_{*\ 1} \quad . \tag{2.7.127}$$

The error in $\tilde{\Phi}_*$

$$\Delta_i \tilde{\Phi}_* = |\tilde{\Phi}_* - \tilde{\Phi}_{*\ i}| \tag{2.7.128}$$

is less than $\Delta_{i,i+1}\tilde{\Phi}_*$ defined by

$$\Delta_{i,i+1}\tilde{\Phi}_* = |\tilde{\Phi}_{*\ i} - \tilde{\Phi}_{i+1}(\tilde{\Psi} = \tilde{\Psi}_i(\tilde{\Phi}_{*\ i}))| \tag{2.7.129}$$

As the estimate for $\Delta_{i,i+1}\tilde{\Phi}_*$ one can take $\Delta_{i,i+1}\tilde{\Phi}_*$ at $\tilde{\Phi}_* = \tilde{\Phi}_{m\ i}$ (i.e. at $\tilde{\Psi}_i = 0$, $\tilde{\Psi}_{i+1} = 0$). Then the third iteration allows to find $\tilde{\Phi}_*$ with the relative error less than $8.63\ 10^{-3}$.

In the considered case one can come to the estimate

$$g(0) < g_1(0) \simeq \frac{\tilde{\Phi}_*}{\bar{\Gamma}} \quad . \tag{2.7.130}$$

So, the relative variation of the supersaturation due to the consumption of the vapor by the homogeneously formed droplets has the order $\bar{\Gamma}^{-1}$. The smallness of $\bar{\Delta}_{\pm} z/y_*$ allows to take into account only the variation of the intensity of the vapor consumption by the droplets and to neglect the variation of the velocity in the expression for y.

The relative variation of the derivative of $\tilde{\Phi}$ on time is equal to

$$\frac{\Delta \frac{d\tilde{\Phi}}{dt}}{\frac{d\tilde{\Phi}}{dt}} = \frac{1-\mu}{\mu\bar{\Gamma}} \quad , \tag{2.7.131}$$

which is small for all μ which are not too small. In the leading term from (2.7.55) it follows that $f_s(\tilde{\Phi}_*)$ is proportional to the forth power of $\tilde{\Psi}$. The variation of $\tilde{\Psi}$ according to the last equation leads to the relative variation of $f_s(\tilde{\Phi}_*)$ of the order

$$\frac{\Delta f_s(\tilde{\Phi}_*)}{f_s(\tilde{\Phi}_*)} \simeq 4\frac{1-\mu}{\mu\bar{\Gamma}} \tag{2.7.132}$$

and to the small variations of $\bar{\Delta}_{\mp} x$

$$\frac{\Delta(\bar{\Delta}_{\mp} x)}{\bar{\Delta}_{\mp} x} \simeq \frac{1-\mu}{\mu\bar{\Gamma}} \quad , \tag{2.7.133}$$

with account of $g(0) \simeq (\bar{\Delta}_{\mp} x)^4 f_s(\tilde{\Phi}_*) \simeq \tilde{\Phi}_*/\bar{\Gamma} \simeq const.$ The influence of the heterogeneously formed droplets is really small.

Consider the validity of (2.7.16), (2.7.19). These conditions can be violated when the relative number of the heterogeneous centers is small. Then the result is known - the total number of the droplets coincides with the total number of the heterogeneous centers. The boundaries of PIFD can be shifted by t_s. As far as this time is much smaller than the time between the heterogeneous formation of the droplets and the homogeneous formation of the droplets this shift doesn't lead to the essential error.

At the period of the homogeneous formation of the droplets (2.7.16), (2.7.19) have to be valid. Consider the case of the moderate influence. Then for the halfwidth of the spectrum one can get

$$\rho_h \simeq \frac{\tilde{\Phi}_*^2}{\bar{\Gamma}\tilde{\Psi}\tau} \quad , \tag{2.7.134}$$

and ρ_s can be estimated as

$$\rho_s = (3 \div 5)(\frac{\tilde{\Phi}_* + 1}{\tilde{\Phi}_*})^{1/3}\bar{\Gamma}^{1/3} \quad . \tag{2.7.135}$$

According to (2.7.70)

$$\tilde{\Psi}\tau \simeq f_s(\tilde{\Phi}_*)^{1/4}\tilde{\Phi}_*^{7/4}\bar{\Gamma}^{-3/4} \quad ,$$

and (2.7.19) can be rewritten as

$$\frac{\tilde{\Phi}_*^{1/4}}{\bar{\Gamma}^{1/4}f_s^{1/4}(\tilde{\Phi}_*)} \gg (3 \div 5)(\frac{\tilde{\Phi}_* + 1}{\tilde{\Phi}_*})^{1/3}\bar{\Gamma}^{1/3} \quad . \tag{2.7.136}$$

The small value of $f_s(\tilde{\Phi}_*)$ due to $\exp(-\bar{F}_{\nu_c})$ ensures the validity of the required inequality. Having taken logarithms from both sides of the last equality and having used the explicit expression for $f_s(\tilde{\Phi}_*)$ one can come to

$$\frac{\ln\tilde{\Phi}_*}{4} - \frac{\ln\bar{\Gamma}}{4} + \frac{a}{12}\rho_c^2 - \frac{\ln a - \ln\pi}{8} - \frac{1}{4}\ln\frac{(\tilde{\Phi}_* + 1)^2}{\tilde{\Phi}_*} \gg \ln(3 \div 5) + \frac{1}{3}\ln\frac{\tilde{\Phi}_* + 1}{\tilde{\Phi}_*} + \frac{\ln\bar{\Gamma}}{3} \quad . \tag{2.7.137}$$

The last equation due to the moderate value of a far from the second order phase transition, $\rho_c \gg 1$, $\bar{\Gamma} \simeq \rho_c^3$ is valid.

The smallness of the relative variation of ζ from $\tilde{\Phi}_*$ allows to express the time t_h of the formation of the halfwidth as

$$t_h = \frac{\rho_h\tau}{\tilde{\Phi}_*} \quad . \tag{2.7.138}$$

With the help (2.7.17), (2.7.134) the inequality (2.7.16) is reduced to

$$\sqrt{8a}\tilde{\Phi}_*^2 \gg (3 \div 5)^3\tilde{\Psi}\tau\bar{\Gamma}^2 \quad . \tag{2.7.139}$$

Then

$$\frac{15}{4}\ln\rho_c \ll \frac{1}{12}\rho_c^2 a \quad . \tag{2.7.140}$$

Due to $\rho_c \gg 1$ one can observe the validity of the last equation.

Consider the situation of the strong influence. The condition (2.7.19) isn't necessary. The validity of (2.7.16) is necessary. The condition $t_s \ll t_h$ with the help of (2.7.138), (2.7.17) can be written in the following form

$$\frac{\rho_s^3}{(\tilde{\Phi}_* + 1)\sqrt{8a}} \ll \frac{\rho_h}{\tilde{\Phi}_*} \tag{2.7.141}$$

and then can be reduced with the help of $\bar{\Gamma} = \rho_c^3 \frac{\tilde{\Phi}_*}{\tilde{\Phi}_*+1}$ to the inequality

$$(3 \div 5)^3 \bar{\Gamma} \ll \rho_h \sqrt{8a} \quad . \tag{2.7.142}$$

So, the condition $t_s \ll t_h$ is stronger than $\rho_s \ll \rho_h$ which can be reduced to

$$(3 \div 5)\bar{\Gamma}^{1/3} \ll \rho_h \quad . \tag{2.7.143}$$

As ρ_h one can take z_h from (2.7.142). Then from (2.7.142) it follows

$$\frac{(3 \div 5)^3 \bar{\Gamma}}{\sqrt{8a}} \ll [\frac{\tilde{\Phi}_* n_\infty}{3\bar{\Gamma}\eta_{tot} y_m}]^{1/2} \quad . \tag{2.7.144}$$

Having noticed that

$$\frac{\eta_{tot} y_m}{n_\infty} = \frac{A\tau}{3 y_m \tilde{\Phi}_m} \quad , \tag{2.7.145}$$

one can come to

$$\frac{(3 \div 5)^6 \bar{\Gamma}^3}{8a} \ll \frac{\tilde{\Phi}_m^2 y_m}{A\tau} \quad . \tag{2.7.146}$$

The experiment is intended to get the values of Φ_* corresponding to the macroscopic conditions. It is intended to get this value without the influence of the heterogeneously formed droplets. Then one can analytically justify the required inequality.

Also one can use the consideration of the previous section and see the approximate compensation of the non stationary effects.

2.7.6 Heterogeneous centers as the obstacle in the experiment

Extract the conditions when it is possible to neglect the influence of the heterogeneous centers.

It is necessary to consider the moderate influence and to solve (2.7.70). Taking into account the explicit expression for $f_s(\tilde{\Phi}_*)$, c one can come to

$$\exp(-\bar{F}_{\nu_c}) = \frac{\tilde{\Phi}_*^2}{(\tilde{\Phi}_*+1)^2}\sqrt{\frac{\pi}{a}}\frac{\bar{\Gamma}^3\tau^4}{6\tilde{\Phi}_*^8}A^4\mu^4\ln 2 \quad . \tag{2.7.147}$$

One has to use $\rho_c^3 \gg 1$ and due to

$$9\ln\rho_c \ll \frac{a}{3}\rho_c^2 \tag{2.7.148}$$

one can neglect $3\ln\bar{\Gamma}$ in comparison with $\bar{F}_{\nu_c}$ in (2.7.147). Then it can be reduced to

$$-\bar{F}_{\nu_c} = 4\ln\mu A\tau \quad . \tag{2.7.149}$$

For ρ_c one can get

$$\rho_c = (-\frac{12}{a}\ln\tau A\mu)^{1/2} \quad . \tag{2.7.150}$$

Due to the macroscopic description the value of $\ln\tau A\mu$ must be negative and big. On the base of ρ_c the value of $\tilde{\Phi}_*$ can be found as

$$\tilde{\Phi}_* = \exp(\frac{2a}{3\rho_c}) - 1 \quad , \tag{2.7.151}$$

which leads due to (2.7.150) to

$$\tilde{\Phi}_* = \exp(\frac{a^{3/2}}{3^{3/2}(-\ln(\mu A\tau))^{1/2}}) - 1 \quad . \tag{2.7.152}$$

The last equation allows to get $\tilde{\Phi}_*$. It can be simplified. Introduce the intensity A_0 corresponding to the boundary of the macroscopic description. Then according to (2.7.150) one can come to

$$A_0 = \frac{\exp(-\frac{a\rho_{c\ 0}^2}{12})}{\tau} \quad , \tag{2.7.153}$$

where $\rho_{c\ 0}$ is approximately equal to $3 \div 4$. The expression (2.7.152) can be rewritten as

$$\tilde{\Phi}_* = \exp(\frac{a^{3/2}}{3^{3/2}(-\ln(A_0\tau))^{1/2}(1+\frac{\ln(\frac{\mu A}{A_0})}{\ln\tau A_0})^{1/2}}) - 1 \quad . \tag{2.7.154}$$

For the wide range of μA the following inequality

$$|\ln\frac{\mu A}{A_0}| \ll |\ln\tau A_0| \tag{2.7.155}$$

is valid. So, in the expression for $\tilde{\Phi}_*$ one can decompose $(1+\frac{\ln(\frac{\mu A}{A_0})}{\ln \tau A_0})^{-1/2}$ in the powers of $\frac{\ln(\frac{\mu A}{A_0})}{\ln \tau A_0}$. In the leading term one can come to

$$\tilde{\Phi}_* = B(\frac{\mu A}{A_0})^C - 1 \quad , \tag{2.7.156}$$

where the constants B and C are defined by

$$B = \exp((\frac{-a^3}{3^3 \ln(A_0 \tau)})^{1/2}) = \exp(\frac{2a}{3\rho_{c\ 0}}) \quad ,$$
$$C = \frac{1}{2}(\frac{-a}{3 \ln \tau A_0})^{3/2} = \frac{4}{\rho^3_{c\ 0}} \quad . \tag{2.7.157}$$

To estimate the influence of the heterogeneous centers one can write the expression for $\tilde{\Psi}$ in the second approximation after the shift of t to t^* with $t = (\Phi(t) - \Phi^*)/A$ taken into account

$$\tilde{\Psi} = A - \frac{3\eta_{tot}}{\tau^3 n_\infty}(\Phi^* \frac{\Phi(t) - \Phi^*}{A} + \frac{A}{2}(\frac{\Phi(t) - \Phi^*}{A})^2)^2 \Phi(t) \quad . \tag{2.7.158}$$

The last equation can be rewritten in the following form

$$\tilde{\Psi} = A - \frac{3\eta_{tot}}{4\tau^3 A^2 n_\infty}(\Phi(t)^2 - \Phi^2_*)^2 \Phi(t) \quad . \tag{2.7.159}$$

According to the weak dependence of $\tilde{\Phi}_*$ on μA one can see that approximately the total number of the droplets is proportional to the intensity of the source in the third power.

Instead of $\tilde{\Phi}_*$ one can take the value of the effective supersaturation at t_* calculated without the consumption of the vapor by the droplets and come to

$$\tilde{\Psi} = A - \frac{3\eta_{tot}}{4\tau^3 A^2 n_\infty}((B(\frac{A}{A_0})^C - 1)^2 - \Phi^{*2})^2 (B(\frac{A}{A_0})^C - 1) \quad . \tag{2.7.160}$$

As far as

$$\frac{\Delta \bar{N}}{\bar{N}} = 3\frac{\Delta \tilde{\Psi}}{\tilde{\Psi}} \quad ,$$

one can come to

$$\frac{\Delta \bar{N}}{\bar{N}} = \frac{9}{4}\frac{\eta_{tot}}{A^3 \tau^3 n_\infty}((B(\frac{A}{A_0})^C - 1)^2 - \Phi^{*2})^2 (B(\frac{A}{A_0})^C - 1) \quad . \tag{2.7.161}$$

The possibility to neglect the influence of the heterogeneous centers can be ensured by the smallness of the r.h.s. of the last equation.

The further evolution of the system can be described by the trivial generalization of the methods presented earlier. One has to stress that now it is necessary to leave the polynomial of the third order for two peaks of the spectrums. But all methods described earlier can be generalized in this way.

Chapter 3

Nucleation in multi component systems

In the previous chapter some model for the phase transition was presented. Now it is necessary to decide whether this model has the common significance. We are going to generalize the presented model[1].

One of the essential restrictions of the previous consideration was the description of the embryo only by one variable ν. The validity of such description is based on the smallness of the characteristic times of the relaxation of other variables in comparison with the time of variation of ν. But the possibility of the existence of the "slow" variables is rather obvious. So, one has to present the generalization for this case also. Moreover, the concrete number of the slow variables is unknown. So, the form of the generalization has to conserve the form of the spectrum. Only in this case the theory will be self consistent. We shall try to get this property.

One can get the estimate for the slowness of this variables. The embryo is the quasi closed object and the rate of collisions with the molecules of the vapor establish the characteristic rate of the variation of the additional variable. There exists also the passive gas and the rate of collisions with these molecules is greater than the already considered one. The rate of relaxation of this variable is at least greater or equal to

[1]We shall call the multi component system as the multidimensional system as far as the kinetic equation in such system is the multidimensional. As far as the dimension of the physical space acts only on some specific constants in the law of the droplets growth it can not lead to misunderstanding.

the relative variation of ν.

So, the most complicate case is the case of the multi component condensation where there are some additional parameters such as the number of the molecules of the different components. The characteristic variations of these variables are similar to the characteristic variation of the total number of the molecules inside the embryos. So, it is the most slow process from the possible ones. As far as it will be shown that in some sense the process of the condensation can be reduced to the one dimensional one then all other possible variables of the embryo description (more rapid ones) will be also included in this picture.

Also it is necessary to announce that the form of the spectrum will be the similar. It gives the opportunity to make some general conclusions with no attention to the concrete number of the variables of the embryo description.

It is evident that the embryo can have some additional parameters which are constant in time. Then the main difficulty lies in the construction of the global picture of the phase transition and this situation is quite analogous to the condensation on the heterogeneous centers with the different activities which is considered in the chapter four.

The investigation of the multi component condensation allows to take into account the discreet character of the evolution. It leads to the certain difficulties but allows to grasp such opportunities for the other possible variables of the embryo description.

The style of construction of the theory here will resemble the already considered case in the ideology. In the construction of the stationary rate of nucleation there appeared many problems and one can not state that this value is determined without errors. But the global evolution will have the same form of the spectrum as in the previous case and the same property of the weak dependence on the microscopic corrections. So, the self consistency of the theory will be restored.

We shall begin from the determination of the stationary rate of nucleation. Earlier this question was investigated in [20] for the mixture of two components where one component has to be under saturated.

The structure of this chapter resembles the structure of the previos chapters. At first we shall stress some problems which don't allow to have the precise expression for the stationary rate of nucleation. Then the system of the condensation equations will be reduced to the situation analogous to the one dimensional case and this will lead to the weak dependence on the microscopic corrections. So, in the first two sections some ideas with the low accuracy can be presented.

3.1 Kinetic equation in the multi component case

3.1.1 Free energy of the embryo formation

Due to the compact character of the embryo of the liquid phase one can consider it in the state of the internal equilibrium.

In the capillarity approximation the free energy of the embryo consists of the volume part and of the surface part. The surface part F_S has the form

$$F_S = S\gamma \quad ,$$

where γ is the surface tension, S is the square of the surface. In the capillarity approximation it is supposed that the surface tension is the surface tension of the plane surface.

The volume part F_V of the free energy F has the form

$$F_V = -\sum_i b_i \nu_i \quad ,$$

where ν_i are the numbers of the molecules of the different components inside the embryo, b_i are the excesses of the chemical potentials in the bulk phase calculated from the saturated case, index i has the values $1, .., m$ for the components in the embryo. The set $\{\nu_i\}$ of the numbers of the different components inside the embryo is the most simple set from the kinetic point of view as far as the numbers of the molecules varies separately in the elementary act of interaction.

The bulk phase is considered in the frames of the capillarity approximation as the homogeneous solution.

For F one can get

$$F = -\sum_i \nu_i b_i + S\gamma \tag{3.1.1}$$

Gibbs-Duhem equations

For b_i one can come in frames of the standard theory of solutions to the following equations

$$b_i = \ln(\frac{n_i}{n_{i\infty}(\xi)}) \ , \tag{3.1.2}$$

where there is the molecule number density of the saturated vapor of the given concentration in the denominator. The concentrations ξ_i of

the component i form the vector ξ. They satisfies to $\sum_i \xi_i = 1$. In the further considerations we shall use the definition ξ for m dimensional vector or for $m-1$ dimensional vector without any special notations.

According to the thermodynamic definitions of the activity coefficients f_i

$$n_{i\infty}(\xi) \equiv n_{i\infty}|_{\xi_i=1}\xi_i f_i(\xi) \quad . \tag{3.1.3}$$

The parts of the chemical potential which depend on these coefficients are the regular functions in the limit situations. This property extracts the activity coefficients.

The activity coefficients satisfy the equations analogous to the Gibbs-Duhem one

$$\sum_a \xi_a d\ln(f_a) = 0 \tag{3.1.4}$$

simply due to the chosen function dependencies. This is the consequence of the expression for the differential of the free energy

$$dF_V = -\sum_i b_i \; d\nu_i \quad .$$

To fulfill the further considerations we have to notice the following very important fact, which will be called as the principle of the correspondence. **The Gibbs-Duhem equation has to be written in the same geometrical construction as the approximation for the free energy.** The problem of the construction of the Gibbs-Duhem equation is connected with the concrete approximation in which the free energy is written. In the capillarity approximation the surface tension is taken as the surface tension of the plane surface. This point has the principal significance. For the spherical embryo the square of the surface is connected with the number of the embryo. For the plane film the square of the surface is the independent parameter. So, in the Gibbs-Duhem equation it has to be considered as the independent one. So, the differential of the free energy can be written as

$$dF = -\sum_i b_i \; d\nu_i + \gamma dS \quad .$$

For the embryo as the object of the Gibbs-Duhem equation it can be written

$$-\sum_i \nu_i d\ln(f_i) + Sd\gamma = 0 \quad . \tag{3.1.5}$$

From the first point of view the natural definition of the concentration is the following one

$$\xi_i = \frac{\nu_i}{\sum_j \nu_j} \quad . \tag{3.1.6}$$

Then

$$\sum_i \xi_i d\ln(f_i) - \tilde{S} d\gamma = 0 \ , \tag{3.1.7}$$

where $\tilde{S} = S/(\sum_i \nu_i)$. As far as the first sum has to go to zero one can get

$$\tilde{S} d\gamma = 0$$

The last equation is rather naive one and is gotten with account of the Gibbs-Duhem equation for the whole embryo which doesn't satisfy to the mentioned principle of the correspondence. Certainly, it is impossible to believe that one can not differentiate the surface tension on the concentration.

The last equation is presented as far as it accumulates the phenomelogical rule of Wilemski and Renninger which forbid to differentiate the surface tension in the expression for the saddle point. The connection with the geometrical aspects of the approximation has not been established earlier. Now we see that this is really the paradox and this paradox is the consequence of the approximation for the free energy.

Note that when the microscopic corrections due to the curvature are taken into account, the Gibbs-Duhem equation must be also corrected in the corresponding terms due to the changed geometry.

The physical reason for the Wilemski-Renninger paradox

The physical reason of the Wilemski-Renninger paradox is existence of the surface layer with the changed concentration. The difference of this concentration from the bulk value compensates the variations of the surface tension. In some naive model one can say that it is profitable for the molecules of some component to move to the surface layer to decrease the surface tension. Certainly, they will move until the moment of some stability when the further variation of the concentration will not lead to decrease of the surface tension, i.e. when the derivative of the surface is equal to zero. Stress again that this qualitative picture is rather naive, but it will open the way to construct the capillarity model with the surface excesses which will be done later.

The difference in the sets of the independent variables in the determination of the saddle point and in the Gibbs-Duhem equation.

Here some certain disadvantages of the mentioned model will be presented. The Gibbs-Duhem equation was derived with account that the chemical potentials are not connected with the number of the molecules of the components in the embryo. But this connection exists and can be taken into account. This account leads to the two different approaches.

Neglect this dependence, i.e. put $(\partial\nu_i/\partial\nu_j) = \delta_{ij}$, and get

$$(\frac{\partial F}{\partial \nu_i}) \mid_{\nu_j \ \xi_j} = -b_i + (\frac{2\gamma}{r}) v_{l \ i} \quad , \tag{3.1.8}$$

where r is the radius of the embryo,

$$v_{l \ i} = (\frac{\partial V}{\partial \nu_i})$$

is the volume for one molecule in the liquid phase, V is the volume of the embryo. Then in the saddle point

$$\frac{b_a(\xi)}{v_{la}} = \frac{b_b(\xi)}{v_{lb}} \quad . \tag{3.1.9}$$

* * *

Express $(\partial\nu_i/\partial\nu_j)$ through the concentrations (due to the finite number of the molecules in the embryo) and get

$$\frac{\partial F}{\partial \nu_i} = -\sum_j b_j \frac{\partial \nu_j}{\partial \nu_i} + \gamma \frac{\partial S}{\partial \nu_i}$$

or

$$\frac{\partial F}{\partial \nu_i} = -\frac{b}{\xi_i} + \gamma \frac{2}{r} \frac{v}{\xi_i} \quad ,$$

where

$$v = \sum_j v_{l \ j} \xi_j \quad ,$$

$$b = \sum_j \xi_j b_j \quad .$$

One and the same equation appears for every component

$$b = \gamma \frac{2}{r} v$$

for the saddle point.

Also there appears the certain difficulty connected with the absence of the connection between the concentrations and the numbers of the molecules in the embryo (the integral definition of the concentration is only some approximation). As a result one can propose the capillarity model with the surface excesses of components

The excesses of the components

To give more justified value of the free energy one can use the formalism of the Gibbs method of the dividing surfaces. The formalism prescribes to put on the considered surface the excesses $\tilde{\nu_i}$ (consider the surface of tension) of the molecules of component i.

Then the concentration can be defined as

$$\xi_i = \frac{\nu_i - \tilde{\nu_i}}{\sum_j (\nu_j - \tilde{\nu_j})} \quad .$$

This leads to

$$-\sum_i \xi_i db_i + \sum_i \frac{\tilde{\nu_i}}{\sum_k (\nu_k - \tilde{\nu_k})} db_i + \frac{S}{\sum_k (\nu_k - \tilde{\nu_k})} d\gamma = 0$$

with the concrete realization

$$-\sum_i \xi_i \frac{db_i}{d\xi_j} + \sum_i \frac{\tilde{\nu_i}}{\sum_k (\nu_k - \tilde{\nu_k})} \frac{db_i}{d\xi_j} + \frac{S}{\sum_k (\nu_k - \tilde{\nu_k})} \frac{d\gamma}{d\xi_j} = 0 \quad .$$

Due to concrete form of the activity coefficients the first term goes to zero and

$$\sum_i \frac{\tilde{\nu_i}}{\sum_k (\nu_k - \tilde{\nu_k})} db_i + \frac{S}{\sum_k (\nu_k - \tilde{\nu_k})} d\gamma = 0$$

with the concrete realization

$$\sum_i \frac{\tilde{\nu_i}}{\sum_k (\nu_k - \tilde{\nu_k})} \frac{db_i}{d\xi_j} + \frac{S}{\sum_k (\nu_k - \tilde{\nu_k})} \frac{d\gamma}{d\xi_j} = 0 \quad .$$

The last relation forms the system of $m - 1$ equations. Then all excesses are defined with one arbitrary constant. This constant can be fixed if the distance between the considered surface and the equimolecular surface is known. It is natural to consider the surface of tension as the basic surface as far as the tension is prescribed only to this surface.

On the level of the differentiates one can get

$$\sum_i (\nu_i - \tilde{\nu_i}) db_i + \sum \tilde{\nu_i} db_i - S d\gamma = 0 \quad .$$

The first sum goes to zero which leads to

$$\sum \tilde{\nu}_i db_i - S d\gamma = 0$$

or

$$\sum_i \frac{\tilde{\nu}_i}{S} db_i = d\gamma \quad .$$

The global structure of the free energy

At first we shall describe the global structure without excesses of the components of the embryo.

In terms of $b(\xi)$ then

$$F = -\nu b(\xi) + S\gamma \quad , \tag{3.1.10}$$

where

$$\nu = \sum \nu_i \quad .$$

To have the condensation it is necessary and sufficient to have the positive values of $b(\xi)$. Introduce

$$B(\xi) = \frac{b(\xi)}{6\pi^{1/2}\gamma^{3/2}v} \quad . \tag{3.1.11}$$

Suppose that the volumes for one molecule depend on the concentration weakly. Introduce

$$\kappa = (S\gamma)^{3/2} = 6\pi^{1/2}\nu\gamma^{3/2}v \quad . \tag{3.1.12}$$

Then

$$F = -\kappa B(\xi) + \kappa^{2/3} \quad . \tag{3.1.13}$$

All channels are the straight lines, they start at the origin of the coordinates of the number of the molecules in the embryo and don't cross. The independent consideration of every channel is possible.

For the characteristics of the saddle point one can get

$$\kappa_m = (\frac{2}{3B(\xi)})^3 \quad , \tag{3.1.14}$$

$$F_m = \kappa_m^{2/3}(\xi)/3 \quad . \tag{3.1.15}$$

Global structure with excesses

Under the macroscopic description

$$\tilde{\nu_a} = \lambda_a S \quad . \tag{3.1.16}$$

Certainly,

$$\lambda_i = \lambda_i(r) \quad .$$

But the application of the Gibbs-Duhem equation for the film requires the plane surface. Then it is necessary to put

$$\lambda_i = \lambda_i(r = \infty) \quad .$$

The mentioned property is the concrete realization of the principle of the "unique curvature": **All surface characteristics and the Gibbs-Duhem equation must be referred to one and the same surface.**

Then

$$F = -\sum_i [b_i(\xi)\xi_i + b_i(\xi)\xi_i \frac{\tilde{\nu_i}}{\nu_i - \tilde{\nu_i}}](\sum_a (\nu_a - \tilde{\nu_a})) + S\gamma \quad . \tag{3.1.17}$$

Let the surface of tension S be the surface around all molecules inside the embryo (to be the equimolecular surface). Then

$$\sum_a (\nu_a - \tilde{\nu_a}) v_{l\ a} = \frac{S^{3/2}}{6\pi^{1/2}} \quad , \tag{3.1.18}$$

$$F = -[\sum_i \xi_i b_i(\xi) + \sum_i \frac{\tilde{\nu_i}}{\nu_i - \tilde{\nu_i}} \xi_i b_i(\xi)] \frac{\kappa}{v 6\pi^{1/2}\gamma^{3/2}} + \kappa^{2/3} \quad . \tag{3.1.19}$$

It is necessary to express ν_i through $S^{3/2}$. Then

$$\frac{\tilde{\nu_i}}{\nu_i - \tilde{\nu_i}} \xi_i = \frac{v 6\pi^{1/2}\gamma^{1/2}}{\kappa^{1/3}} \lambda_i \quad . \tag{3.1.20}$$

For the free energy one can approximately get

$$F = -[\sum_i \xi_i b_i(\xi)] \frac{\kappa}{v 6\pi^{1/2}\gamma^{3/2}} + \kappa^{2/3}[1 - \frac{\sum_i \lambda_i b_i(\xi)}{\gamma}] \quad . \tag{3.1.21}$$

We have the same analytical structure as the already observed one after the shifts

$$\kappa^{2/3} \to \kappa^{2/3}[1 - \frac{\sum_i \lambda_i b_i(\xi)}{\gamma}] \quad ,$$

$$B \to B = \frac{[\sum_i \xi_i b_i(\xi)]}{v 6\pi^{1/2}\gamma^{3/2}[1 - \frac{\sum_i \lambda_i b_i(\xi)}{\gamma}]^{3/2}} \quad .$$

This model satisfies all necessary requirements of the self consistency.

Note that sometimes only the extremal value of the intensive parameter (concentration) in the bulk liquid is known. It leads to the certain difficulties discussed in the first chapter.

3.1.2 The small parameters of the kinetic theory

The small parameters of the classical nucleation theory are expressed in the following inequalities

$$\nu_c^{-1} \ll 1 \quad , \quad \frac{\Delta\nu_c}{\nu_c} \ll 1 \quad , \quad (\Delta\nu_c)^{-1} \ll 1 \quad .$$

The first inequality is necessary to the macroscopic description of the critical embryo. All other inequalities can be derived for the homogeneous condensation from the first one. The second inequality allows to consider some weak functions as W^+ as constants. The third inequality allows to come to the differential form of the kinetic equation and for the homogeneous free energy it allows to come to the Fokker-Planck approximation.

We shall establish these inequalities in the multidimensional case.

Here we are going to establish only some strong inequalities which put only some weak requirement of the accuracy of our constructions.

To apply the standard theory of the solutions it is necessary to have

$$\nu_i \gg 1$$

for every component or we have to consider the liquid phase in the field of few rare molecules, which is almost impossible to do analytically.

The result of the previous inequalities is

$$\kappa_c \gg 1 \quad .$$

Hierarchical inequalities

Transform to κ, ξ_i or to the linearized deviations of these variables from the values at the saddle point.

Due to

$$B(\xi)|_{\xi_i=0} = \infty \quad , \quad B(\xi)|_{\xi_i=1} = -\infty \tag{3.1.22}$$

the channel of nucleation can not be at $\xi_i \sim 1$ and $\xi_i \sim 0$. Then

$$\xi_i \sim 1 - \xi_i \sim 1 \quad . \tag{3.1.23}$$

One can introduce the linearized deviations υ and μ_i according to

$$\upsilon = \sum_a (\frac{\partial \kappa}{\partial \nu_a})_c (\nu_a - \nu_{ac}) \quad , \tag{3.1.24}$$

$$\mu_i = \sum_a (\frac{\partial \xi_i}{\partial \nu_a})_c (\nu_a - \nu_{ac}) \quad . \tag{3.1.25}$$

The critical region is defined by the inequality $|F - F_c| \leq 1$. Then for the derivatives one can get

$$(\frac{\partial F}{\partial \xi_i})_c = 0 \quad , \quad (\frac{\partial F}{\partial \kappa})_c = 0 \quad , \tag{3.1.26}$$

$$(\frac{\partial^2 F}{\partial \xi_i^2})_c = -B''(\xi)\kappa \quad , \quad (\frac{\partial^2 F}{\partial \kappa^2})_c = -2\kappa^{-4/3}/9 \quad , \tag{3.1.27}$$

$$(\frac{\partial^2 F}{\partial \kappa \partial \xi_i})_c = 0 \quad . \tag{3.1.28}$$

The value of $B''(\xi)$ can be reasonably estimated without any big or small parameters.

Introduce the halfwidhts $\Delta\kappa$ and $\Delta\xi_i$ of the critical region

$$\Delta_c \kappa = [\frac{2}{|\frac{\partial^2 F}{\partial \kappa^2}|_c}]^{1/2} \quad , \tag{3.1.29}$$

$$\Delta_c \xi_i = [\frac{2}{|\frac{\partial^2 F}{\partial \xi_i^2}|_c}]^{1/2} \quad . \tag{3.1.30}$$

For the orders of the magnitudes one can get

$$\Delta_c \kappa \sim \kappa^{2/3} \quad , \quad \Delta_c \xi_i \sim \kappa^{-1/2} \quad .$$

Then

$$\frac{\Delta_c \kappa}{\kappa} \ll 1 \quad , \quad \frac{\Delta_c \xi_i}{\xi_i} \ll 1 \quad ,$$

where the values are taken in the saddle point. These inequalities are analogous to the second inequality in the classical theory.

Introduce the variations $\delta_i\kappa$ and $\delta_i\xi_a$ in the elementary act of absorption (or ejection). Consider that all W_a^+ have one and the same order and one can omit the index of the component. Then[2]

$$\delta_i\kappa \sim 1 \quad , \quad \delta_i\xi_a \sim \kappa^{-1} - \xi_a\kappa^{-1} \quad .$$

So, one can come to

$$\frac{\delta_i\kappa}{\Delta_c\kappa} \ll 1 \quad , \qquad \frac{\delta_i\xi_a}{\Delta_c\xi_i} \ll 1 \quad .$$

These inequalities are analogous to the third inequality in the classical theory.

These estimates allow to state that

1. There is an equilibrium along ξ.
2. The kinetic equation can be reduced to the differential form.
3. The decompositions on κ can be restricted at the second derivative.
4. For the rather wide class of $B(\xi)$ one can use the Fokker-Planck approximation.

The last statement depends on the behavior of B. The further consideration will be devoted to the special cases where these statements aren't valid.

In the multidimensional situation one can establish some additional inequalities.

The characteristic times t_κ, t_{ξ_i} of the relaxation to the stationary state in the near critical region along κ and ξ_i are the following

$$t_\kappa \sim \frac{\Delta_c\kappa}{\delta_i\kappa}\frac{1}{W_i^+} \quad , \qquad t_{\xi_i} \sim \frac{\Delta_c\xi_i}{\delta_a\xi_i}\frac{1}{W_a^+} \quad .$$

For the orders of the magnitudes one can have

$$t_\kappa \sim \kappa^{4/3} \quad , \qquad t_{\xi_i} \sim \kappa \quad .$$

Then

$$\frac{t_{\xi_i}}{t_\kappa} \sim \kappa^{-1/3} \ll 1 \quad .$$

Then κ is the slow variable and all other variables are the rapid ones. The solution can be simplified.

Kinetic equation in ν_i.

Construct the kinetic equation in the Fokker-Plank approximation.

[2]It is sufficient that at very small W_a^+ the concentrations ξ_a are not too small.

Introduce the distribution function $n(\nu_a, t)$ normalized on the number of the droplets in the unit volume. For $n(\nu_a, t)$ it is easy to write the kinetic equation in the following form

$$\frac{\partial n}{\partial t} = \sum_a W_a^+ n(\nu_a - 1, \nu_b) - W_a^-(\nu_a) n(\nu_a, \nu_b) - \\ W_a^+ n(\nu_a, \nu_b) + W_a^-(\nu_a + 1) n(\nu_a + 1, \nu_b) \quad . \tag{3.1.31}$$

The adsorption coefficients can be found from the gas kinetic theory as

$$W_i^+ = \alpha_{ki} n_i v_{Ti} S/4 \quad , \tag{3.1.32}$$

where n_i is the molecules number density in the vapor, v_{Ti} is the mean thermal velocity, α_{ki} is the condensation coefficient, S is the square of the surface[3]. One can also get the equations of the detailed balance

$$W_i^-(\nu_i + 1) = W_i^+(\nu_i) \exp(\frac{\partial F(\{\nu_a\})}{\partial \nu_i}) \quad . \tag{3.1.33}$$

Consider (3.1.31) in the form close to the equilibrium. Then it can be written in the form of the balance equation

$$\frac{\partial n}{\partial t} = -\sum_a \frac{\partial J_a}{\partial \nu_a} \quad , \tag{3.1.34}$$

where

$$J_a = W_a^+ n(\nu_a, \{\nu_b\}) - W_a^-(\nu_a + 1) n(\nu_a + 1, \{\nu_b\}) \tag{3.1.35}$$

is the component of the flow.

Use the function

$$f(\{\nu_a\}) = \frac{n(\{\nu_a\})}{n^e(\{\nu_a\})} \quad , \tag{3.1.36}$$

where there is the equilibrium distribution in the denominator. Then

$$\frac{\partial n}{\partial t} = -\sum_a \frac{\partial}{\partial \nu_a} [W_a^+ n^e(\nu_a, \{\nu_b\})(f(\nu_a, \{\nu_b\}) - f(\nu_a + 1, \{\nu_b\}))] \quad . \tag{3.1.37}$$

[3]The surface can differ from the surface of tension which leads to corrections.

In the Fokker-Planck approximation it goes to

$$\frac{\partial n}{\partial t} = \sum_a \frac{\partial}{\partial \nu_a}[W_a^+ n^e(\{\nu_b\}) \frac{\partial}{\partial \nu_a} f(\{\nu_b\})] \quad . \tag{3.1.38}$$

or

$$\frac{\partial n}{\partial t} = \sum_a \frac{\partial}{\partial \nu_a} W_a^+ [\frac{\partial}{\partial \nu_a} n(\{\nu_b\}) + \frac{\partial F}{\partial \nu_a} n(\{\nu_b\})] \quad . \tag{3.1.39}$$

Now it is necessary to formulate the boundary conditions. When ξ deviates from ξ_c and F grows until $F - F_c = 1$ one can show that n is small in comparison with n_c^e and there is no flow across these boundaries. Near the line $F = F_c - 1$ which separates the critical region from the pre-critical one there is the equilibrium distribution. Near the opposite line $F = F_c - 1$ which separates the critical region from the post critical one the distribution has to be negligible in comparison with the equilibrium one. This corresponds to the absence of the inverse flow.

One can show the weak dependence of the solution to the concrete position of the boundaries[4].

Also one can show the weak dependence of the solution on the cut off of the asymptotes of the formal near critical refion (along the lines $F = F_c$) of the lines $F = F_c + 1$ and $F = F_c - 1$. It isn't necessary to require the stationary state there[5]. æ

The hierarchy can be made even more strong by the cancel of the cross term in κ and in ξ_i) by the appropriate choice of the variables. At the same time one has to conserve the square form of the free energy

$$F = F_c + \sum_i y_i^2 - x^2 \quad , \tag{3.1.40}$$

$$y_i = (\frac{\partial^2 F}{\partial \xi_i^2})^{1/2} \mu_i \quad ,$$

$$x = (\frac{\partial^2 F}{\partial \upsilon^2})^{1/2} \upsilon \quad .$$

The Lorenz transformation [56] considered in the first chapter conserve the form of (3.1.40). With the special choice of the parameter of this transformation one can chancel the cross term in the kinetic equation.

[4]In one dimension as far as in the multidimensional situation.

[5]It is necessary to do only when the flow goes near this line. It seems to be only in the special situation.

The value of $B''(\xi)$ is rather arbitrary. If B'' contains the small parameter then $t_{\xi_i} \sim B''(\xi)^{-1}\kappa$. When in the order $B''(\xi) > \kappa^{-1/3}$ there is the quasi equilibrium over the stable variables. In the opposite situation $B'' < \kappa^{-1/3}$ one can see the independent nucleation under the different constant values of this characteristics which are the quasi integrals of the evolution. Nontrivial interaction appears in the global kinetics of the process. One can call the different values of this parameter as the different sorts of the heterogeneous centers. The most complicate variant of the theory taking into account the exhausting of the heterogeneous centers is described in the chapter four[6].

3.1.3 Kinetic equation in the form of the finite differences

Kinetic equation in υ, μ_i.

In the elementary absorption of the molecule

$$\mu \to \mu + \delta_a \mu \quad , \quad \nu \to \nu + \delta_a \nu \quad , \tag{3.1.41}$$

where the absence of index marks that for all components we have the same equations.

Transform in (3.1.31) to υ and μ

$$\frac{\partial n}{\partial t} = \sum_i \{[W_i^+ n(\upsilon - \delta_i\upsilon, \mu - \delta_i\mu) - W_i^-(\upsilon,\mu)n(\upsilon,\mu)] - \\ [W_i^+ n(\upsilon,\mu) - W_i^-(\upsilon + \delta_i\upsilon, \mu + \delta_i\mu)n(\upsilon + \delta_i\upsilon, \mu + \delta_i\mu)]\} \quad . \tag{3.1.42}$$

The vector μ has the components μ_j. The arguments for W_i^- are presented due to the sharp dependence on υ and μ. This dependence can be found from the equations of the detailed balance

$$W_i^-(\upsilon,\mu) = W_i^+ \frac{n^e(\upsilon - \delta_i\upsilon, \mu - \delta_i\mu)}{n^e(\upsilon,\mu)} \quad , \tag{3.1.43}$$

where n^e is the equilibrium distribution. Then one can come to

$$\frac{\partial n}{\partial t} = \sum_i W_i^+ [\{n(\upsilon - \delta_i\upsilon, \mu - \delta_i\mu) - \frac{n^e(\upsilon - \delta_i\upsilon, \mu - \delta_i\mu)}{n^e(\upsilon,\mu)}$$

[6] It is necessary to change the linear exponent on activity on the gaussian and fulfill the integration over this distribution. All constructions will be absolutely analogous but there will be no problems with the convergence.

(3.1.44)

$$n(\upsilon,\mu)\} - \{n(\upsilon,\mu) - \frac{n^e(\upsilon,\mu)}{n^e(\upsilon+\delta_i\upsilon,\mu+\delta_i\mu)} n(\upsilon+\delta_i\upsilon,\mu+\delta_i\mu)\}] \quad .$$

Transform in (3.1.42) from the function $n(\upsilon,\mu)$ to the function $f = n/n^e$. This function is more smooth and has the very simple boundary conditions. Then

$$\frac{\partial n}{\partial t} = \sum_i W_i^+ \{n^e(\upsilon-\delta_i\upsilon,\mu-\delta_i\mu)[f(\upsilon-\delta_i\upsilon,\mu-\delta_i\mu) - f(\upsilon,\mu)] \tag{3.1.45}$$

$$-n^e(\upsilon,\mu)[f(\upsilon,\mu) - f(\upsilon+\delta_i\upsilon,\mu+\delta_i\mu)]\} \quad .$$

Operators of connection

The last equation can be presented in the following form

$$\frac{\partial n}{\partial t} = \sum_i W_i^+ \{(T_i(\upsilon-\delta_i\upsilon,\mu) - T_i(\upsilon,\mu)) + (T_i(\upsilon,\mu) - T_i(\upsilon,\mu+\delta_i\mu))\} \quad , \tag{3.1.46}$$

where

$$T_i(\upsilon,\mu) = n^e(\upsilon,\mu-\delta_i\mu)[f(\upsilon,\mu-\delta_i\mu) - f(\upsilon+\delta_i\upsilon,\mu)] \quad . \tag{3.1.47}$$

After the transformation from the finite differences to the derivatives one can come to

$$\frac{\partial n}{\partial t} = \sum_i W_i^+ \{\sum_{j=1}^{\infty} \frac{(-1)^j(\delta_i\upsilon)^j}{j!} \frac{\partial^j}{\partial\upsilon^j} T_i(\upsilon,\mu) - \sum_{j=1}^{\infty} \frac{(\delta_i\mu)^j}{j!} \frac{\partial^j}{\partial\mu^j} T_i(\upsilon,\mu)\} \quad . \tag{3.1.48}$$

Rewrite the expression for $T_i(\upsilon,\mu)$ through $n^e(\upsilon,\mu)$ ($f(\upsilon,\mu)$. There appeared many derivatives in transition from $n^e(\upsilon,\mu)$ to $n^e(\upsilon,\mu-\delta_i\mu)$. Then one can change μ and ν. Then instead of (3.1.46), (3.1.47) one can get

$$\frac{\partial n}{\partial t} = \sum_i W_i^+ \{(T_i(\upsilon,\mu-\delta_i\mu) - T_i(\upsilon,\mu)) + (T_i(\upsilon,\mu) - T_i(\upsilon+\delta_i\upsilon,\mu))\} \quad , \tag{3.1.49}$$

where

$$T_i(\upsilon,\mu) = n^e(\upsilon-\delta_i\upsilon,\mu)[f(\upsilon-\delta_i\upsilon,\mu) - f(\upsilon,\mu+\delta_i\mu)] \quad . \tag{3.1.50}$$

The kinetic equation can be reduced to

$$\frac{\partial n}{\partial t} = \sum_i W_i^+ \{\sum_{j=1}^{\infty} \frac{(-1)^j (\delta_i \mu)^j}{j!} \frac{\partial^j}{\partial \mu^j} T_i(\upsilon, \mu) - \sum_{j=1}^{\infty} \frac{(-1)^j (\delta_i \upsilon)^j}{j!} \frac{\partial^j}{\partial \upsilon^j} T_i(\upsilon, \mu)\} \quad . \tag{3.1.51}$$

After decomposition of the first term of (3.1.50) one can get

$$T_i(\upsilon, \mu) = [\sum_{j=0}^{\infty} \frac{(-1)^j (\delta_i \upsilon)^j}{j!} \frac{\partial^j}{\partial^j \upsilon} n^e(\upsilon, \mu)][f(\upsilon - \delta_i \upsilon, \mu) - f(\upsilon, \mu + \delta_i \mu)] \quad . \tag{3.1.52}$$

After decomposition of the other terms one can come to

$$T_i(\upsilon, \mu) = [\sum_{j=1}^{\infty} \frac{(-1)^j (\delta_i \upsilon)^j}{j!} \frac{\partial^j}{\partial \upsilon^j} n^e(\upsilon, \mu)] [\sum_{j=1}^{\infty} \frac{(-1)^j (\delta_i \upsilon)^j}{j!} \frac{\partial^j}{\partial \upsilon^j} f(\upsilon, \mu) - \sum_{j=0}^{\infty} \frac{(\delta_i \mu)^j}{j!} \frac{\partial^j}{\partial \mu^j} f(\upsilon, \mu)] \quad . \tag{3.1.53}$$

We have not taken into account the multidimensioness of the vector of the concentration. All the derivaties mentioned here must be imagined as the corresponding terms in the decompositions in the Tailor series. As far as the scale on concentrations of the different components is one and the same it doesn't lead to the missing of the essential features of the description.

Extraction of the main operator

Due to $\xi_i \sim 1 - \xi_i$ one can get

$$\delta_i \mu \sim \delta_i \upsilon / \kappa_c \quad . \tag{3.1.54}$$

Determine the characteristic scale of f. It corresponds to the characteristic sizes of the critical region and with the halfwidhts[7] of the equilibrium distribution. Then in application to f

$$\frac{\partial}{\partial \mu_i} \simeq (\Delta \mu_i)^{-1} \quad , \quad \frac{\partial}{\partial \upsilon} \simeq (\Delta \upsilon)^{-1} \quad . \tag{3.1.55}$$

[7]The halfwidhts in υ, μ_i correspond to the halfwidhts in κ, ξ_i.

Taking into account $\xi_i \sim 1 - \xi_i$ one can get

$$\delta_i \mu \frac{\partial}{\partial \mu} \simeq \kappa_c^{-1/2} \quad , \quad \delta_i \upsilon \frac{\partial}{\partial \upsilon} \simeq \kappa_c^{-2/3} \quad . \tag{3.1.56}$$

Now one can extract in (3.1.51) the main operator. Having left in the r.h.s. of kinetic equation the main operator[8] one can get

$$\frac{\partial n}{\partial t} = \sum_i W_i^+ \sum_{j=1}^{\infty} \frac{(-1)^j (\delta_i \mu)^j}{j!} \frac{\partial^j}{\partial \mu^j} T_i(\upsilon, \mu) \quad . \tag{3.1.57}$$

For $T_i(\upsilon, \mu)$ in the leading term one can get

$$T_i(\upsilon, \mu) = n^e(\upsilon, \mu)[-\sum_{j=1}^{\infty} \frac{(\delta_i \mu)^j}{j!} \frac{\partial^j}{\partial \mu^j} f(\upsilon, \mu)] \quad . \tag{3.1.58}$$

In the stationary case having restricted by the finite number of derivatives one can get the linear differential equation with the constant coefficients and the well known solution.

Iteration solution of kinetic equation

Return to the finite differences and get

$$\frac{\partial n}{\partial t} = \sum_i W_i^+ (T_i(\upsilon, \mu - \delta_i \mu) - T_i(\upsilon, \mu)) \quad , \tag{3.1.59}$$

$$T_i(\upsilon, \mu) = n^e(\upsilon, \mu)[f(\upsilon, \mu) - f(\upsilon, \mu + \delta_i \mu)] \quad . \tag{3.1.60}$$

In the stationary case the solution is the evident - it is the equilibrium distribution on μ, i.e. $f(\upsilon, \mu) = f(\upsilon)$.

Return to f and get

$$\frac{\partial n}{\partial t} = \sum_i W_i^+ [n^e(\upsilon, \mu - \delta_i \mu) \tag{3.1.61}$$
$$[f(\upsilon, \mu - \delta_i \mu) - f(\upsilon, \mu)] - n^e(\upsilon, \mu)[f(\upsilon, \mu) - f(\upsilon, \mu_i + \delta \mu)]] \quad .$$

or

$$\frac{\partial n}{\partial t} = \sum_i [W_i^+ [(n(\upsilon, \mu - \delta_i \mu) \tag{3.1.62}$$
$$-n(\upsilon, \mu) \exp(F(\upsilon, \mu) - F(\upsilon, \mu - \delta_i \mu))] - [n(\upsilon, \mu) - n(\upsilon, \mu + \delta_i \mu) \exp(F(\upsilon, \mu + \delta_i \mu) - F(\upsilon, \mu))]] \quad .$$

[8] The high derivatives are also conserved due to the arbitrary behavior of B.

In the last two equations the terms for the evolution along μ_i are extracted. One can consider only the equations (3.1.59)-(3.1.62) but the evolution only along μ_i can not lead to the flow of the embryos. The formation of the flow occurs due to correction terms in the kinetic equation.

One can analytically reproduce all results of the section devoted to the nonstationary effects. Then only the stationary case is interesting.

The ideology of the current consideration is to show that the true solution can be attained only after a rather big number of iterations.

Rewrite the kinetic equation in the following form

$$\frac{\partial n}{\partial t} = \Lambda n + Dn \quad , \tag{3.1.63}$$

where Λ is the r.h.s. of (3.1.62) which is the main operator and D is additional operator. Even the simplest iteration scheme

$$\Lambda n_{i+1} = \frac{\partial n_i}{\partial t} - Dn_i \quad , \tag{3.1.64}$$

where i is the number of the iteration and the zero approximation is the solution of (3.1.62), requires the inversion of Λ.

In the case of the narrow channel the discrete character of the domain of $n(v, \mu)$ is very essential. All differential forms of the kinetic equation have the sense in continuous domain of the distribution.

The difficulty appears also in the definition of T_i on the base of Λn. One has to determine m functions T_i with the connection according to (3.1.60) at the level of f.

The split of the reconstruction of n on the base of Λn is impossible. This split takes place only when one of the kinetic coefficients is big. This case is essential due to the condition of essential variation of the rate of nucleation[9]. Then the sum over i disappears and one can come to the recurrent relation

$$\frac{\Lambda n + W_i^+ T_i(v, \mu - \delta_i \mu)}{W_i^+} = T_i(v, \mu) \quad . \tag{3.1.65}$$

Equation (3.1.60) is now the recurrent relation for f as function of μ.

The recurrent relation defines T_i and f with the arbitrary normalizing factor. This factor has to be given in the previous iteration approximation[10].

[9] The kinetic equation is effectively the binary one.

[10] See the next sections.

Discrete character of the number of the molecules

The transition to the continuous form is valid only under validity of one of the following inequalities[11]

$$\frac{\delta_a \mu_i}{\Delta \mu_i} \ll 1 \quad . \tag{3.1.66}$$

for all i.

Consider some interval along υ from υ_0 to $\upsilon_0 + \bar{\Delta}\upsilon$ and choose $\bar{\Delta}\upsilon$ in such a way that the set $\{\nu_a\}$ with υ, from this interval as function of μ_i for all i is rather dense. So, the maximum distance between two neighbor μ_i is many times less than the halfwidht of the critical region over μ_i.

At the same time $\bar{\Delta}\upsilon$ is rather small

$$\frac{\bar{\Delta}\upsilon}{\Delta\upsilon} \ll 1 \quad . \tag{3.1.67}$$

So, one can use the effective averaging over the interval $[\upsilon_0, \upsilon_0 + \bar{\Delta}\upsilon]$.

The narrow channel

Consider the very narrow channel when the embryos have to move by one trajectory with the minimal free energy $F_m(\upsilon)$. The trajectory in the plane of the variables is the broken line. The function F_m can be presented also as the broken line with the nodes with effective integer coordinates greater than $min(F)$ over μ_i.

In approximation of the equilibrium over μ the expression for the flow I^s along υ has the following form

$$I^{s^{-1}} = \frac{1}{\tilde{N}} \sum_{-\Delta\upsilon}^{\Delta\upsilon} \frac{\exp(F_m(\upsilon))}{W^+} \quad , \tag{3.1.68}$$

where W^+ plays the role of the kinetic coefficient along the line of the stepens descent[12] and $\tilde{N}$ is the normalizing factor of the equilibrium distribution on υ.

From the last equation it follows

$$I^{s^{-1}} = \frac{1}{\tilde{N} W^+} \int_{-\infty}^{\infty} \exp(min_\mu F) \exp(F_m - min_\mu F) \lambda d\upsilon \quad , \tag{3.1.69}$$

[11] If the kinetic coefficients aren't too small.

[12] It can be used only for estimates. At every step of the trajectory one has to use the kinetic coefficient W^+ corresponding to the addition of the necessary component. Now it is impossible to remove it from the integral.

where λ is the rather smooth function. It appears from the transition from the discrete steps to the integration over v. It is rather easy to calculate λ on the base of the given trajectory.

After the split of the whole trajectory into some intervals with the size $\bar{\Delta}v$ one can get

$$I^{s^{-1}} = \frac{1}{\tilde{N}W^+} \sum_{bands} \int_{v_0}^{v_0+\bar{\Delta}v} \lambda \exp(min_\mu F) \exp(F_m - min_\mu F) dv \quad , \tag{3.1.70}$$

$$I^{s^{-1}} = \frac{1}{\tilde{N}W^+} \sum_{bands} \exp(min_\mu F) \int_{v_0}^{v_0+\bar{\Delta}v} \lambda \exp(F_m - min_\mu F) dv \quad . \tag{3.1.71}$$

Having returned to the summation over v one can come to

$$I^{s^{-1}} = \frac{1}{\tilde{N}W^+} \sum_{v} (\bar{\Delta}v)^{-1} \exp(min_\mu F) \int_{v_0}^{v_0+\bar{\Delta}v} \exp(F_m - min_\mu F) dv \quad . \tag{3.1.72}$$

The integral in the r.h.s. depends weakly on the position of the interval in the critical region and one can come to

$$I^{s^{-1}} = \frac{1}{\tilde{N}W^+} C \sum_{v} \exp(min_\mu F) \quad , \tag{3.1.73}$$

where

$$C = (\bar{\Delta}v)^{-1} \int_{v_0}^{v_0+\bar{\Delta}v} \exp(F_m - min_\mu F) dv \tag{3.1.74}$$

practically doesn't depend on v and can be considered as a rescaling factor. The value λ can be included[13] in W^+.

Calculate C. Then

$$C = << \exp(F_m - min_\mu F) >> \quad , \tag{3.1.75}$$

where $<<\quad>>$ denotes the average value of the function. Supposing that the points $\{\nu_i\}$ cover the interval $[-\Delta\mu, \Delta\mu]$ homogeneously[14] we transform in the calculation of C from the integration over v to the integration over μ. In some situations (corresponding to the rotation on the angles with the rational cosines) there is no dense coverage. These

[13] The values W^+ and λ have to be unified already in the first expression.

[14] It corresponds to the homogeneous behavior of W^+ and λ.

situations can be described by the analytical expansions of the expression from the situations with the dense coverage.

Then

$$C = \frac{1}{2\bar{\Delta}\mu}\int_{-\bar{\Delta}\mu}^{\bar{\Delta}\mu}\exp(F_m - min_\mu F)d\mu \simeq \frac{1}{\bar{\Delta}\mu}\int_0^{\bar{\Delta}\mu}\exp(\frac{|\frac{\partial^2 F}{\partial\mu_i^2}|\mu}{\bar{\Delta}\mu})^2 d\mu \quad , \tag{3.1.76}$$

where $\bar{\Delta}\mu$ corresponds to the half of variation of μ in the elementary act and the integration is imagined in the following sense

$$\bar{\Delta}\mu \Leftrightarrow \delta_a\mu \quad , \tag{3.1.77}$$

$$\int_0^{\bar{\Delta}\mu} \Leftrightarrow [\sum_b W_b^+]^{-1}\Pi_a W_a^+ \int_0^{\delta_a\mu} \quad . \tag{3.1.78}$$

This gives the method to calculate of C.

Approximation of the mean value of the free energy

Apply the approximation of the mean value of the free energy and get

$$I^{s^{-1}} = \frac{1}{\tilde{N}W^+}\sum_{-\Delta\upsilon}^{\Delta\upsilon}\exp(\tilde{F}(\upsilon)) \quad , \tag{3.1.79}$$

where

$$\tilde{F}(\upsilon) = \frac{\sum_{j=0}^{\infty} F(\upsilon, \mu + j\bar{\Delta}\mu)\exp(-F(\upsilon, \mu + j\bar{\Delta}\mu))}{\sum_{j=0}^{\infty}\exp(-F(\upsilon, \mu + j\bar{\Delta}\mu))} \quad . \tag{3.1.80}$$

In the case of the very narrow channel there remains only one term and

$$\tilde{F} = F_m(\upsilon) \quad . \tag{3.1.81}$$

Then

$$I^{s^{-1}} = \frac{1}{\tilde{N}W^+}\sum_{-\delta\upsilon}^{\delta\upsilon}\exp(min_\mu F)\exp(F_m - min_\mu F) \quad . \tag{3.1.82}$$

The case of the wide channel

Calculate $\tilde{F}$

$$\tilde{F} = \frac{\int_{-\infty}^{\infty} F\exp(-F)d\mu}{\int_{-\infty}^{\infty}\exp(-F)d\mu} \quad . \tag{3.1.83}$$

With the square approximation for F as the function of μ one can get

$$\tilde{F} = F + \frac{1}{2}(m-1) \quad , \tag{3.1.84}$$

where m is the number of components. The additional term $1/2$ is constant and has to be excluded as far as the activation barrier is the difference between two values of the free energy.

æ

Approximations for connection between T_i

When the connection between T_i is known the kinetic equation is closed. Establish this connection from (3.1.60). Having substituted the first derivative instead of the finite differences one can get

$$T_b(\mu) = T_a(\mu)\frac{||\delta_b\mu||}{||\delta_a\mu||} \quad . \tag{3.1.85}$$

Then this relation becomes the equation for the function T_a. It is reasonable to choose T_i for the more rapid component.

On the base of T_a one can find f from (3.1.60):

$$\frac{T_a(\mu)}{n^e(\mu)} = f(\mu) - f(\mu + \delta_a\mu) \quad . \tag{3.1.86}$$

This equation can be easily solved in the finite differences or with the restriction by the finite number of the derivatives.

Really, the connection (3.1.85) is too approximate. One can correct it. Suppose that the approximation f_j to the solution f of equation $\Lambda f = g$ is known. Then we know $g_j = \Lambda f_j$. Then

$$g - g_j = \Lambda f - \Lambda f_j = \sum_i W_i^+ \{T_i(\mu - \delta_i\mu) - T_i(\mu) - T_{ij}(\mu - \delta_i\mu) + T_{ij}(\mu)\} \quad , \tag{3.1.87}$$

where

$$T_{ij} = n^e(\mu)[f_j(\mu) - f_j(\mu + \delta_i\mu)] \quad . \tag{3.1.88}$$

Present the connection between $T_i - T_{ij}$ in the following form

$$T_i - T_{ij} \simeq [\frac{f(\mu) - f_j(\mu)}{f_j(\mu)} - \frac{f(\mu + \delta_i\mu) - f_j(\mu + \delta_i\mu)}{f_j(\mu + \delta_i\mu)}]f_j(\mu)n^e(\mu) \quad . \tag{3.1.89}$$

Introduce the function

$$\varphi_j(\mu) = \frac{f(\mu) - f_j(\mu)}{f_j(\mu)} \tag{3.1.90}$$

and present (3.1.89) in the following form

$$T_i(\mu) - T_{ij}(\mu) = [\varphi_j(\mu) - \varphi_j(\mu + \delta_i\mu)] f_j(\mu) n^e(\mu) \quad . \tag{3.1.91}$$

Then

$$\frac{T_a(\mu) - T_{aj}(\mu)}{||\delta_a\mu||} = \frac{T_b(\mu) - T_{bj}(\mu)}{||\delta_b\mu||} \quad , \tag{3.1.92}$$

$$g - g_j = \sum_b W_b^+ \frac{||\delta_b\mu||}{||\delta_a\mu||} (T_a(\mu - \delta_a\mu) - T_a(\mu) - T_{aj}(\mu - \delta_a\mu) + T_{aj}(\mu)) \quad . \tag{3.1.93}$$

The last equation is the recurrent relation to find T_a. Due to the approximate character of (3.1.92) we get only some approximation to the solution of $g = \Lambda f$.

One can construct on the every solution the pseudo equilibrium distribution

$$n_j^q = f_j n^e(\mu) \tag{3.1.94}$$

and the effective free energy

$$F_{eff}^j(\mu) = -\ln(n_j^q(\mu)/\tilde{N}) + const \tag{3.1.95}$$

($\tilde{N}$ is the normalizing factor).

3.1.4 Initial approximation

Approximation of the equilibrium.

The main operator has the eigenfunction corresponding to the zero eigenvalue. This function is the equilibrium distribution on μ. All other eigenvalues are the negative ones which ensures the relaxation to the equilibrium. Then

$$n(\upsilon, \mu) = n(\upsilon) n^e(\mu) \quad , \tag{3.1.96}$$

$$n^e(\mu) = \tilde{N} \exp(-F(\upsilon, \mu)) \quad . \tag{3.1.97}$$

This approximation doesn't take into account the evolution on υ.

Rewrite (3.1.31) as

$$\frac{\partial n}{\partial t} = Ln \quad , \tag{3.1.98}$$

where L is the operator of the r.h.s. Introduce operator P of the reduction to the local in υ form. It reduces all arguments to one υ.

It is evident that

$$PL = \Lambda \tag{3.1.99}$$

and the solution of the equation

$$P\frac{\partial}{\partial t}n^* = PLn^* \tag{3.1.100}$$

coincides with n^e from (3.1.97).

Kinetic equation under smooth dependence on υ.

One can substitute the finite differences along υ by the first derivatives. Then

$$T_i(\upsilon,\mu) = n^e(\upsilon-\delta_i\upsilon,\mu)(-\delta_i\upsilon\frac{\partial f(\upsilon,\mu)}{\partial\upsilon} - f(\upsilon,\mu+\delta_i\mu) + f(\upsilon,\mu)) \quad . \tag{3.1.101}$$

One can use this approximation in the equilibrium function

$$n^e(\upsilon-\delta_i\upsilon,\mu) = n^e(\upsilon,\mu)(1+\delta_i\upsilon\frac{\partial F(\upsilon,\mu)}{\partial\upsilon}) \quad . \tag{3.1.102}$$

Then

$$\frac{\partial n}{\partial t} = \sum_i W_i^+\{(T_i(\upsilon,\mu-\delta_i\mu) - T_i(\upsilon,\mu)) - \frac{\partial T_i(\upsilon,\mu)}{\partial\upsilon}\delta_i\upsilon\} \quad . \tag{3.1.103}$$

There are three sorts of terms: the terms without derivatives on υ, the terms with one operator $\partial/\partial\upsilon$, the terms with two operators $\partial/\partial\upsilon$.

The restriction by the terms without derivatives on υ leads to (3.1.59), (3.1.60). The restriction by the terms with no more than one operator $\partial/\partial\upsilon$ leads only to the regular growth and can not lead to the overcoming of the activation barrier.

Corrections of the initial approximation

Now one has to formulate some simple ways to construct the initial approximation which is rather close to the real solution.

Due to the observed hierarchy the critical region is stretched along υ and the angles between the flow and the axis are known ν_i.

Effective free energy

One can imagine J_i/n as the probability for the embryo to get the transition[15]. Then after the integration over υ

$$\frac{\partial n(\mu)}{\partial t} = \sum_i \frac{J_i}{n(\upsilon)}[n(\mu-\delta_i\mu) - n(\mu)] \quad , \tag{3.1.104}$$

[15]Suppose it to be the smooth function of μ_i.

where J_i is the component of the flow along ν_i. After the decomposition of PL one can come to

$$\frac{\partial n(\mu)}{\partial t} = \sum_i \{(W_i^+ + \frac{J_i}{n(\upsilon)})n(\mu - \delta_i\mu) - W_i^-(\mu)n(\mu)\} - \sum_i \{(W_i^+ + \frac{J_i}{n(\upsilon)})n(\mu) + W_i^-(\mu + \delta_i\mu)n(\mu + \delta_i\mu)\} \quad . \tag{3.1.105}$$

Rewrite the equation of the detailed balance

$$0 = \sum_i (W_i^+ + \frac{J_i}{n(\upsilon)})n^e(\mu - \delta_i\mu) - W_i^- n^e(\mu) \quad .$$

In the terms of the effective free energy $\tilde{F}$ one can come to

$$0 = \sum_i (W_i^+ + \frac{J_i}{n(\upsilon)}) \exp(-\tilde{F}(\mu - \delta_i\mu)) - W_i^- \exp(-\tilde{F}(\mu)) \quad . \tag{3.1.106}$$

For the real free energy one can get

$$0 = \sum_i (W_i^+) \exp(-F(\mu - \delta_i\mu)) - W_i^- \exp(-F(\mu)) \quad .$$

In the terms of the derivatives one can come to

$$0 = \sum_i (W_i^+ + \frac{J_i}{n(\upsilon)}) \exp(\sum_j \frac{\partial \tilde{F}}{\partial \mu_j}\delta_i\mu_j) - W_i^- \quad ,$$

$$0 = \sum_i W_i^+ \exp(\sum_j \frac{\partial F}{\partial \mu_j}\delta_i\mu_j) - W_i^- \quad .$$

Then

$$0 = \sum_i (W_i^+ + \frac{J_i}{n(\upsilon)}) \exp(\sum_j \frac{\partial \tilde{F}}{\partial \mu_j}\delta_i\mu_j) - W_i^+ \exp(\sum_j \frac{\partial F}{\partial \mu_j}\delta_i\mu_j) \quad .$$

After the decomposition of the exponents one can come to

$$0 = \sum_i W_i^+ (\sum_j \frac{\partial \tilde{F}}{\partial \mu_j}\delta_i\mu_j - \sum_j \frac{\partial F}{\partial \mu_j}\delta_i\mu_j) + \frac{J_i}{n(\upsilon)}(1 + \sum_j \frac{\partial \tilde{F}}{\partial \mu_j}\delta_i\mu_j) \quad .$$

Then

$$\frac{J_i}{n(\upsilon)} \gg \frac{J_i}{n(\upsilon)} \sum_j \frac{\partial \tilde{F}}{\partial \mu_j} \delta_i \mu_j \quad .$$

It allows to present the detailed balance equation in the following form

$$0 = \sum_j (\sum_i W_i^+ \delta_i \mu_j)(\frac{\partial \tilde{F}}{\partial \mu_j} - \frac{\partial F}{\partial \mu_j}) + \sum_i \frac{J_i}{n(\upsilon)} \quad .$$

One can derive the last formula in the way

$$0 = \sum_i W_i^+ \exp(\sum_j \frac{\tilde{F}}{\mu_j} \delta_i \mu_j)(1 - \exp(-\sum_j \frac{\partial F}{\partial \mu_j} \delta_i \mu_j + \sum_j \frac{\partial \tilde{F}}{\partial \mu_j} \delta_i \mu_j)) + \frac{J_i}{n(\upsilon)} \exp(\sum_j \frac{\partial \tilde{F}}{\partial \mu_j} \delta_i \mu_j) \quad . \tag{3.1.107}$$

The exponent from the difference of the derivatives can be decomposed under more weak restrictions on the width of the critical region. Then

$$0 = \sum_i W_i^+ \exp(\sum_j \frac{\tilde{F}}{\mu_j} \delta_i \mu_j) \sum_j (\frac{\partial F}{\partial \mu_j} \delta_i \mu_j - \frac{\partial \tilde{F}}{\partial \mu_j} \delta_i \mu_j) - \frac{J_i}{n(\upsilon)} \exp(\sum_j \frac{\partial F}{\partial \mu_j} \delta_i \mu_j) \quad ,$$

which leads to the previous relation.

One can put

$$J_i = l_i J \quad ,$$

where l_i are known even without the precise value of the flow. Then

$$\sum_j c_{1j} \frac{\partial F}{\partial \mu_j} - \frac{\partial \tilde{F}}{\partial \mu_j} = \frac{J}{n(\upsilon)} \quad ,$$

where

$$c_{1j} = \frac{\sum_i W_i^+ \delta_i \mu_j}{\sum_i l_i}$$

is the constant.

The detailed balance equations have to be observed for every component. After the integration one can come to

$$\tilde{F} = F - \sum_j \frac{J}{n(v)} c_{1j}\mu_j + c_2 \quad ,$$

where c_2 is the constant of the integration.

The minimum of the effective free energy is attained at μ_0 from equation

$$\frac{\partial F}{\partial \mu_j}|_{\mu_j=\mu_{0j}} = \frac{J}{n(v)} c_{1j} \quad .$$

The pseudo equilibrium distribution will be

$$n^e \simeq \exp(-\tilde{F})\tilde{N} \quad . \tag{3.1.108}$$

Square approximation

The square approximation for the free energy as the function of μ

$$F = \sum_j (\frac{\mu_j}{\Delta\mu_j})^2$$

is also valid for the effective free energy

$$\tilde{F} = \sum_j (\frac{\mu_j - \mu_{0j}}{\Delta\mu_j})^2$$

with the same $\Delta\mu$. For μ_0 one can get

$$\mu_{0j} = c_{1j}\frac{J}{n(v)}\frac{(\Delta\mu_j)^2}{2} \quad .$$

Note that the transformation to diagonalize the square forms (and the force matrix) for the free energy and for the effective free energy may be different.

The effective quasi equilibrium distribution under the square form of the free energy can be written as

$$n^e \simeq \tilde{N}\exp(-\sum_j (\frac{\mu - \mu_{0j}}{\Delta\mu_j})^2) \tag{3.1.109}$$

with $\Delta\mu = \{\Delta\mu_j\}$. It allows to introduce the conception of the trajectory of the embryos in the critical region $\mu_0(v) = \{\mu_{0j}(v)\}$. Note that

μ_0 coincides with the average μ on the quasi equilibrium distribution determined by the last equation.

Even when the square approximation for the real free energy isn't valid it can be applied for the effective free energy

$$\tilde{F} = \tilde{F}(\mu_0(\upsilon)) + \sum_j \frac{\partial^2 F}{\partial \mu_j^2}|_{\mu_j=\mu_{0j}}(\mu_j - \mu_{0j})^2 \quad . \tag{3.1.110}$$

So, one can introduce the quasi local Lorenz transformation.

In the rough approximation

$$J_0 = -W^+ \frac{\partial F(\upsilon, \mu = 0)}{\partial \upsilon} n - W^+ \frac{\partial n}{\partial \upsilon} \quad , \tag{3.1.111}$$

where W^+ is the corresponding kinetic coefficient.

Rescaling of the flow

In terms of the densities of the saturated vapors one can get

$$\frac{\partial \tilde{F}}{\partial \upsilon} = \ln \frac{\varpi_\upsilon(\mu = \mu_0)}{\varpi} \quad ,$$

$$\frac{\partial F}{\partial \upsilon} = \ln \frac{\varpi_\upsilon(\mu = 0)}{\varpi} \quad ,$$

where ϖ is the density of the vapor, ϖ_υ is the density of the vapor saturated over the embryo with the size υ.

Then

$$\frac{\partial \tilde{F}}{\partial \upsilon} - \frac{\partial F}{\partial \upsilon} = \ln \frac{\varpi_\upsilon(\mu = \mu_0)}{\varpi_\upsilon(\mu = 0)} \quad .$$

Linearize the chemical potential from the concentration corresponding to the equilibrium one for the free energy up to the concentration corresponding to the equilibrium one for the effective free energy.

As far as the chemical potential for the ideal gas is the logarithm of the density we shall linearize the logarithm of the density. Then

$$\ln \varpi_\upsilon(\mu = \mu_0) = \ln \varpi_\upsilon(\mu = 0) + \sum_a c_{2a}\mu_a \quad .$$

It leads to

$$\frac{\partial \tilde{F}}{\partial \upsilon} - \frac{\partial F}{\partial \upsilon} = \sum_a c_{2a}\mu_a \quad .$$

Rewrite the expression for the flow as

$$J_\upsilon = -W^+ \frac{\partial \tilde{F}}{\partial \upsilon} n(\upsilon) - W^+ \frac{\partial n}{\partial \upsilon} \quad .$$

Substitute the square approximation and get

$$J_\upsilon = -W^+ \frac{\partial F}{\partial \upsilon} n(\upsilon) - W^+ \sum_a c_{1a} c_{2a} J \frac{(\Delta \mu_a)^2}{2} - W^+ \frac{\partial n}{\partial \upsilon} \quad .$$

It leads to the rescaling of the flow

$$J = \frac{J_0}{1 + k_1} \quad ,$$

where

$$k_1 = W^+ \sum_a c_{1a} c_{2a} \frac{(\Delta \mu_a)^2}{2} \quad .$$

Trajectories

Introduce the derivative $d^{tr}/d^{tr}\upsilon$ along the trajectory. As far as the critical region is stretched along υ, the value of effective W^+ is well defined. The free energy along the trajectory is more smooth than earlier.

Then

$$\frac{d^{tr} F}{d^{tr} \upsilon} = \frac{\partial F}{\partial \upsilon} + \sum_a \frac{\partial F}{\partial \mu_a} |_{\mu_a = \mu_{0a}} \frac{\partial \mu_a}{\partial \upsilon} \quad .$$

Write the effective kinetic equation along the trajectory

$$J_{\mu_0} = -W^+ \frac{\partial F}{\partial \upsilon} n_{\mu_0} - \frac{n_{\mu_0}}{n(\upsilon)} \frac{\partial \mu_0}{\partial \upsilon} J_{\mu_0} W^+ \sum_a c_{1a} \frac{\partial \mu_a}{\partial \upsilon} - W^+ \frac{\partial n_{\mu_0}}{\partial \upsilon} \quad .$$

Taking into account

$$n_{\mu_0} = n(\upsilon) \frac{d\upsilon}{d\mu_0} \quad ,$$

one can come to

$$J_{\mu_0} = -W^+ \frac{\partial F}{\partial \upsilon} n_{\mu_0} + J_{\mu_0} k_2 - W^+ \frac{\partial n_{\mu_0}}{\partial \upsilon}$$

with the constant value of

$$k_2 = W^+ \sum_a c_{1a} \frac{\partial \mu_a}{\partial \upsilon} \quad .$$

Then one can come to the following rescaling

$$J = \frac{J_0}{1 + k_2} \quad . \tag{3.1.112}$$

Nonisothermal nucleation

Earlier the possibility for the appearance of the embryo with the low temperature was not considered. According to thermodynamic fluctuations the probability w of the deviation of the temperature of the embryo from the temperature of the media by ΔT is given by

$$w \simeq \exp(-c_v \nu \frac{(\Delta T)^2}{2T^2}) \quad , \tag{3.1.113}$$

where c_v is the heat capacity per one molecule at the fixed volume, ν is the number of the molecules inside the embryo.

With the help of the Klipeiron - Klausius equation one can get

$$F_c(\Delta T) = \frac{1}{3} a (\frac{2a}{3(b(T_0) - \beta \Delta T / T_0)})^2 + \frac{c_v}{2T^2} (\frac{2a}{3(b(T_0) - \beta \Delta T / T_0)})^3 (\Delta T)^2 \quad . \tag{3.1.114}$$

For small ΔT one can get

$$F_c(\Delta T) = F_c(0) + \beta \frac{\Delta T}{T_0} (\frac{2a}{3b(T_0)})^3 + \frac{a \beta^2 (\Delta T_0)^2}{b^2(T_0) T_0^2} (\frac{2a}{3b(T_0)})^2 + \frac{c_v}{2T^2} (\frac{2a}{3b(T_0)})^3 (\Delta T)^2 \quad . \tag{3.1.115}$$

Then F as the function of ΔT has minimum at some negative ΔT.

The more precise way is to find the minimum of the free energy as the function of two variables - of the temperature and of the number of the molecules inside the embryo

$$F(\nu, \Delta T) = a \nu^{2/3} - (b(T_0) - \beta \frac{\Delta T}{T_0}) \nu + \frac{c_\nu}{2T^2} \nu (\Delta T)^2 \quad .$$

It can be reduced to the old definition with the rescaling

$$b \to b(T_0) - \beta \frac{\Delta T}{T_0} - \frac{c_\nu}{2T^2} (\Delta T)^2$$

when the surface tension depends on the temperature weakly.

For the critical embryo

$$\nu_c^{1/3} = \frac{2a}{3[b(T_0) - \beta\frac{\Delta T}{T_0} - \frac{c_\nu}{2T^2}(\Delta T)^2]} \quad ,$$

$$F_c = \frac{a}{3}\nu_c^{2/3} \quad .$$

For the deviation of the temperature one can get

$$\Delta T = -\frac{T_0\beta}{c_\nu} \quad ,$$

which solves the problem.

Take into account the dependence of the surface tension on the temperature. Then

$$\nu_c^{1/3} = \frac{2a(T_0 + \Delta T)}{3[b(T_0) - \beta\frac{\Delta T}{T_0} - \frac{c_\nu}{2T^2}(\Delta T)^2]} \quad .$$

It is necessary to get the extremum of

$$F_c = \frac{a(T_0 + \Delta T)}{3}[\frac{2a(T_0 + \Delta T)}{3[b(T_0) - \beta\frac{\Delta T}{T_0} - \frac{c_\nu}{2T^2}(\Delta T)^2]}]^2 \quad .$$

* * *

Here the temperature is the ordinary thermodynamic parameter. The Klipeiron-Klausius equation appeared after the approximation of the constant value of the heat capacity of the condensation and isn't too specific for the temperature. So, all considerations can be repeated for the other thermodynamic parameter.

* * *

The construction of the initial approximation is also important as far as it allows to simplify the kinetic equation.

The main difficulty of the kinetic equations the existence of the great quantity of the high order derivatives. The consideration of the stationary conditions leads to the constant values of the flow expressed through T_i. Then the functions T_i are very smooth. The finite derivatives there can be substituted by the first derivatives. Another source of the high order derivatives is the decomposition of the finite differences of f. Along

v the possibility to keep only the first derivative is ensured by the geometrical size of the critical region. Along μ there is the equilibrium which leads f to *const* $f(v)$.

One can make the accuracy more high by the redefinition of f as the ratio of the real distribution to the quasi equilibrium distribution, which is established at every step of the iteration procedure.

Also one can use the coordinates ν_a, $\mu_{b\neq a}$. It will be useful for the situation with the rapid component. But even without the rapid component the variable ν_a will be the slow one and $\mu_{b\neq a}$ will be the rapid one.

3.2 Different approximations

3.2.1 Square approximation

One can put $n^e(v-\delta_i v,\mu)=n^e(v,\mu)$ due to the big width of the critical region along v. Then in the main approximation it follows

$$\frac{\partial n}{\partial t}=\sum_i W_i^+(\sum_{a\ b}(\delta\mu_a)(\delta\mu_b)\frac{\partial}{\partial\mu_a}n^e\frac{\partial}{\partial\mu_b}f+(\delta v)^2\frac{\partial}{\partial v}n^e\frac{\partial}{\partial v}f+ \\ \sum_a(\delta_i\mu_a)(\delta_i v)\frac{\partial}{\partial\mu_a}n^e\frac{\partial}{\partial v}f+\sum_a(\delta_i\mu_a)(\delta_i v)\frac{\partial}{\partial v}n^e\frac{\partial}{\partial\mu_a}f) \quad . \tag{3.2.1}$$

In terms of the free energy one can get

$$\frac{\partial n}{\partial t}=\sum_i W_i^+(\sum_{a\ b}\frac{\partial}{\partial\mu_a}[\frac{\partial}{\partial\mu_b}n+\frac{n}{n^e}\frac{\partial}{\partial\mu_b}n^e](\delta\mu_a)(\delta\mu_b) \\ +\sum_a\frac{\partial}{\partial\mu_a}[\frac{\partial}{\partial v}n-\frac{n}{n^e}\frac{\partial}{\partial v}n^e](\delta\mu_a)(\delta v) \\ +\sum_a\frac{\partial}{\partial v}[\frac{\partial}{\partial\mu_a}n-\frac{n}{n^e}\frac{\partial}{\partial\mu_a}n^e](\delta\mu_a)(\delta v) \\ +\frac{\partial}{\partial v}[\frac{\partial}{\partial v}n-\frac{n}{n^e}\frac{\partial}{\partial v}n^e](\delta v)^2) \quad . \tag{3.2.2}$$

Using the evident relations

$$\frac{1}{n^e}\frac{\partial}{\partial\mu_a}n^e=-\frac{\partial F}{\partial\mu_a} \quad , \quad \frac{1}{n^e}\frac{\partial}{\partial v}n^e=-\frac{\partial F}{\partial v} \quad , \tag{3.2.3}$$

one can have

$$\frac{\partial n}{\partial t} = \sum_i W_i^+ (\sum_{a\ b} \frac{\partial}{\partial \mu_a}[\frac{\partial}{\partial \mu_b} n + n\frac{\partial F}{\partial \mu_b}](\delta_i \mu_a)(\delta_i \mu_b) + \sum_a [\frac{\partial}{\partial \upsilon}[\frac{\partial}{\partial \mu_a} n + n\frac{\partial F}{\partial \mu_a}] + \frac{\partial}{\partial \mu_a}[\frac{\partial}{\partial \upsilon} n + n\frac{\partial F}{\partial \upsilon}]](\delta_i \mu_a)(\delta_i \upsilon) + \frac{\partial}{\partial \upsilon}[\frac{\partial}{\partial \upsilon} n + n\frac{\partial F}{\partial \upsilon}](\delta_i \upsilon)^2) \quad . \tag{3.2.4}$$

In the square approximation for the free energy

$$|\frac{\partial F}{\partial \mu_a}| \simeq \frac{2\mu_a}{\Delta \mu_a^2} \quad , \quad |\frac{\partial F}{\partial \upsilon}| \simeq \frac{2\upsilon}{\Delta \upsilon^2} \quad , \tag{3.2.5}$$

where it is taken into account that $\upsilon = 0$ and $\mu = 0$.

Split of the main operator

In the square approximation one can come to the following kinetic equation

$$\frac{\partial n}{\partial t} = \sum_i W_i^+ \{\sum_{a\ b} \frac{\partial}{\partial \mu_a}[\frac{\partial}{\partial \mu_b} n + n\frac{2\mu_b}{\Delta \mu_b^2}](\delta_i \mu_a)(\delta_i \mu_b) + \sum_a [\frac{\partial}{\partial \upsilon}[\frac{\partial}{\partial \mu_a} n + n\frac{2\mu_a}{\Delta \mu_a^2}] + \frac{\partial}{\partial \mu_a}[\frac{\partial}{\partial \upsilon} n - n\frac{2\upsilon}{\Delta \upsilon^2}]](\delta_i \upsilon)(\delta_i \mu_a) + \frac{\partial}{\partial \upsilon}[\frac{\partial}{\partial \upsilon} n - n\frac{2\upsilon}{\Delta \upsilon^2}](\delta_i \upsilon)^2)\} \quad . \tag{3.2.6}$$

The operator of the r.h.s. will be denoted as Λ.

The channel of nucleation is the straight line $\mu = const$ on the plane κ, μ. Then the Lorenz transformation vanishes the cross term

$$\sum_a [\frac{\partial}{\partial \upsilon}[\frac{\partial}{\partial \mu_a} n + n\frac{2\mu_a}{\Delta \mu_a^2}] + \frac{\partial}{\partial \mu_a}[\frac{\partial}{\partial \upsilon} n - n\frac{2\upsilon}{\Delta \upsilon^2}]](\delta_i \upsilon)(\delta_i \mu_a) = \Lambda_{\upsilon\mu} \ , \tag{3.2.7}$$

and there are no terms of such a nature.

Contrary to the other parts of the theory the choice of the Lorenz transformation is specific in the multidimensional case in comparison with the binary case. The parameter α (with components α_i) of the Lorenz transformation is the root of the algebraic equation of the power m (there are m components). To determine α one can take into account the small value of this parameter. Really, under the Lorenz transformation υ transforms to $\upsilon \pm \sum_i \alpha_i \mu_i$. But υ must be the unstable variable.

Then in the order of the magnitude

$$\alpha_a < \frac{\Delta\mu_a}{\Delta\upsilon} \quad . \tag{3.2.8}$$

But one can come to

$$\frac{\Delta\mu_a}{\Delta\upsilon} \ll 1 \quad . \tag{3.2.9}$$

It is easy to find the small root of the algebraic equation.

After the Lorenz transformation

$$\Lambda = \Lambda_\upsilon + \Lambda_\mu \quad , \tag{3.2.10}$$

where

$$\Lambda_\mu = \sum_{a\ b} c_{\mu_a\ \mu_b}(\frac{\partial}{\partial\mu_a}(c_{\mu_b}\mu_b + \frac{\partial}{\partial\mu_b})) \quad , \tag{3.2.11}$$

$$\Lambda_\upsilon = c_\upsilon(\frac{\partial}{\partial\upsilon}(-c'_\upsilon\upsilon + \frac{\partial}{\partial\upsilon})) \tag{3.2.12}$$

and $c_{\mu_a\mu_b}$, c_{μ_b}, c_υ are some known constants. After the separation of the stable variables and the reduction of the square forms to the sums of squares one can come to

$$\Lambda = \Lambda_\mu + \Lambda_\upsilon \quad ,$$

where

$$\Lambda_\mu = \sum_a \tilde{c}_{\mu_a}(\frac{\partial}{\partial\mu_a}(2\mu_a + \frac{\partial}{\partial\mu_a})) \quad ,$$

$$\Lambda_\upsilon = \tilde{c}_\upsilon(\frac{\partial}{\partial\upsilon}(-2\upsilon + \frac{\partial}{\partial\upsilon})) \quad ,$$

where $\tilde{c}_\upsilon$, $\tilde{c}_{\mu_a}$ are some known constants and the rescaling of the variables has been done. Note

$$\Lambda_\mu = \sum_a \Lambda_{\mu_a} \quad ,$$

where

$$\Lambda_{\mu_a} = \tilde{c}_{\mu_a}(\frac{\partial}{\partial\mu_a}(2\mu_a + \frac{\partial}{\partial\mu_a})) \quad .$$

Kinetic equation can be rewritten in the following way

$$\frac{\partial n}{\partial t} = (\Lambda + A)n \quad , \tag{3.2.13}$$

where A completes Λ until the r.h.s. of the kinetic equation.

It is necessary to construct the eigenvalues and eigenfunctions of Λ.

Eigenfunctions

Return to the function analogous to f. The role of the equilibrium distribution is played by $n^e \simeq \exp(-\mu^2)/\tilde{N}$. Then

$$\Lambda_{\mu_a} n^e f(\mu) = n^e \hat{\Lambda}_{\mu_a} f(\mu) \quad . \tag{3.2.14}$$

Determine $\hat{\Lambda}_{\mu_a}$:

$$\hat{\Lambda}_{\mu_a} = \tilde{c}_{\mu_a}(\frac{\partial}{\partial \mu_a} - 2\mu_a)\frac{\partial}{\partial \mu_a} \quad . \tag{3.2.15}$$

The function f is extracted by the simple form of the boundary conditions

$$f(\mu_a) \to 0 \ , \quad |\mu_a| \to \infty \quad . \tag{3.2.16}$$

The eigenfunctions of $\hat{\Lambda}_{\mu_a}(x)$ with the boundary conditions mentioned above are the Hermit polinomials

$$H_n(x) = (-1)^n \exp(x^2)\frac{d^n}{dx^n}\exp(-x^2) \quad n = 0, 1, 2, 3, ... \quad .$$

They satisfy to the following relations

$$\frac{d}{dx}H_n(x) = 2nH_{n-1}(x) \quad , \tag{3.2.17}$$

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x) \quad , \tag{3.2.18}$$

$$H_{n+1}(x) = (2x - \frac{\partial}{\partial x})H_n(x) \quad . \tag{3.2.19}$$

The eigenvalues of this operator are

$$\lambda_n = -2n \quad n = 0, 1, 2, 3, ... \quad . \tag{3.2.20}$$

The eigenfunctions of $\hat{\Lambda}_\mu$ allow to construct the solution. Rewrite the kinetic equation in the following form

$$n^e \frac{\partial f}{\partial t} = n^e \hat{L} f \quad . \tag{3.2.21}$$

Having extracted the operator $\hat{\Lambda}_\mu = \sum_a \hat{\Lambda}_{\mu_a}$ one can get

$$\frac{\partial f}{\partial t} = \hat{\Lambda}_\mu f + \hat{A}_\mu f \quad , \tag{3.2.22}$$

where

$$\hat{A}_\mu = \hat{L} - \hat{\Lambda}_\mu \tag{3.2.23}$$

is small in comparison with $\hat{\Lambda}_\mu$. In the initial moments one can neglect $\hat{A}_\mu$. Then as far as the eigenfunctions of operator $\hat{\Lambda}_\mu$ are known the equation can be solved

$$f(\upsilon,\mu) = \sum_a \sum_m < f(\mu, t=0), H_m(\mu_a) > \exp(\lambda_m t \tilde{c}_{\mu_a}) H_m(\mu_a) \quad . \tag{3.2.24}$$

The symbol $< .,. >$ defines the scalar product

$$< p, q >= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} p(x) q(x) \exp(-x^2) dx \quad . \tag{3.2.25}$$

Note that

$$< H_m, H_n > \simeq \delta_{nm} m! 2^m \quad . \tag{3.2.26}$$

After some time

$$f(\mu,\upsilon) \to \sum_a < f(\mu, t=0), H_0(\mu_a) > H_0(\mu_a) = f_0(\mu) \quad . \tag{3.2.27}$$

Iterations

As far as H_0 is the eigenfunction with the zero eigenvalue the operator $\hat{\Lambda}_\mu$ after some time isn't the main in application to f.

Principally there exists two opportunities to construct iterations. In the first approach the operator $\frac{\partial}{\partial t}$ is included in the main operator. The iterations are defined as

$$\frac{\partial f_i}{\partial t} = \hat{\Lambda}_\mu f_i + \hat{A}_\mu f_{i-1} \quad . \tag{3.2.28}$$

One can take for initial approximation $f_0(\mu)$. After the projection of the last equation on H_m one can get the differential equation which allow the analytical solution. This solution can be presented as the decomposition on the Hermit polinomials

$$f = \sum_b \sum_m a_{m\ b}(t) H_m(\mu_b) \quad . \tag{3.2.29}$$

The important property is the possibility to write the additional operator as the superposition of the operators of the increase a^+ and the

decrease a^- of the number level (the number of the eigenfunction). The simple form of operators

$$a_b^- = \frac{\partial}{\partial \mu_b} \quad , \quad a_b^+ = (2\mu_b - \frac{\partial}{\partial \mu_b}) \tag{3.2.30}$$

allows to rewrite the additional operator as the superposition of these operators.

The explicit form of the solution of the differential equation leads to the complicate dependence on time. Then the initial dependence $a_0(t)$ is spread on the all levels and is very complicate.

The second approach is rather more simple[16]

$$\frac{\partial f_{i-1}}{\partial t} = \hat{\Lambda}_\mu f_i + \hat{A}_\mu f_{i-1} \quad . \tag{3.2.31}$$

The initial approximation is f_0. One can calculate these iterations analytically at every step. But in the time dependence there are no new effects due to the next iteration approximation. As the result one has to reconsider the time depndence in the effective self consistent way based on the new functional form of the current approximation to the solution. It can be done in many approximate ways, at this step there will be no analitical difficulties.

Here in fact the Chapman-Enskog method can be used.

The time dependence in this approach is presented through the dependence of a_0 on t. Having projected the kinetic equation on H_0 one can get

$$\frac{\partial f_{i-1}}{\partial t} = P_0 \hat{A}_\mu f_{i-1} \quad , \tag{3.2.32}$$

which gives the explicit expression for the derivative on time. In the last equation $P_0 \sim \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} ....H_0(x) \exp(-x^2) dx$. The dependence of a_0 on time determines the derivative on time which is necessary to calculate the next approximation.

The high levels are not so localized on μ. It is reasonable to restrict the consideration by the levels which have the size of localization less than Δv.

Diagrams and the renormalization

The combinations a^+a^- and a^-a^+ can be directly included in the main operator because they have the same eigenfunctions. The eigenvalues of the operator will be changed but the zero value will be conserved. The evolution of the solution can be drawn as the broken line

[16] Both methods are valid for the arbitrary form of $\hat{\Lambda}_\mu$.

with the nodes in the integer values of the coordinates (i.e. on some levels). Certainly, all trajectories have to start at the zero point.

What type of trajectories will be important in the calculation of the flow. The flow has almost the same direction as v has. So, it is necessary to get one of the components of the flow j_v. To calculate the number of the droplets one have to know the integral flow along v:

$$J_v^{int} = \sum_a \int_{-\infty}^{\infty} d\mu_a j_v(\mu) \quad . \tag{3.2.33}$$

Integration on μ_a correspond to the projection on $H_0(\mu_a)$. Then only the trajectories with the end at the zero level has the contribution in the flow.

One can suggest some methods of simplification of the diagrams. One can introduce the "dressed" node. The dressed node on the level j is the sum of the trajectories with the start and the end at the this level. In the terms of the dressed nodes every trajectory has only one peak. We are interested in the dressed node of the zero level[17].

One can also write some equations of the connection between the values of the dressed nodes in a very simple form.

Matrix of transitions

The intensities γ_{pq} of transitions from the level p to the level q doesn't depend on the number of the iteration approximation. Then the amplitudes a_p in the decomposition of f on the Hermit polinomials are connected by

$$a_p = \sum_q \gamma_{pq} a_q \quad .$$

Then the vector of amplitudes is the eigenvector of the matrix of transitions with the eigenvalue 1.

To define this eigenvector of the matrix $\Gamma = \{\gamma_{pq}\}$ split $\Gamma - I$ (I is the unit matrix) into the sum of the upper triangle matrix Γ_+ and lower triangle matrix Γ_-. In Γ_+ there are the coefficients of operators of the decrease of the level. The matrix Γ_- consists of the coefficients of the increase of the level. According to (3.2.17), (3.2.18) the coefficients which are increasing with the increase of the level can be found only in[18] Γ_+. That's why Γ_- is small in comparison with Γ_+. So, the iteration approach $\Gamma_+ a_q^{(i+1)} + \Gamma_- a_q^{(i)} = 0$ with the corresponding rescaling is rather

[17] In the calculation one has to know the nodes at the other levels.

[18] The existence of the coefficients increasing with the number of the level leads to the asymptotic character of iteration seria with the absence of the convergence.

effective. One can easy inverse the triangle matrices and calculate every step of this procedure.

Unstable variable

Generalize this approach by the inclusion of Λ_υ. After the rescaling of υ one can come to (3.2.12):

$$\Lambda_\upsilon \exp(\upsilon^2) f = \exp(\upsilon^2)\hat{\Lambda}_\upsilon f \quad , \tag{3.2.34}$$

where

$$\hat{\Lambda}_\upsilon = \tilde{c}_\upsilon(2\upsilon + \frac{\partial}{\partial\upsilon})\frac{\partial}{\partial\upsilon} \quad . \tag{3.2.35}$$

The eigenvalues of Λ_υ with the boundary conditions of the vanishing at ∞ are the following ones

$$\lambda_n = 2n \quad , \quad n \geq 0 \quad , \tag{3.2.36}$$

and the eigenfunctions can be presented in the following form

$$f_n = const\ i^n erfc(\upsilon) \quad . \tag{3.2.37}$$

The functions $i^n erfc(\upsilon)$ under the integer n are

$$i^n erfc(\upsilon) = \int_\upsilon^\infty i^{n-1} erfc(x)dx \quad , \tag{3.2.38}$$

$$i^0 erfc(\upsilon) = erfc(\upsilon) \sim \int_\upsilon^\infty \exp(-x^2)dx \quad , \tag{3.2.39}$$

and under the real n they can be expressed through the functions of the parabolic cylinder

$$i^n erfc(\upsilon) = \exp(-\upsilon^2/2)\frac{D_{n+1/2}(\upsilon 2^{1/2})}{(2^{n-1}\pi)^{1/2}} \quad . \tag{3.2.40}$$

The normalizing constants can be chosen from the asymptotes

$$f_n \to 0 \quad \upsilon \to \infty \quad ; \quad f_n \to \frac{2|\upsilon|^n}{\Gamma(n+1)} \quad \upsilon \to -\infty \tag{3.2.41}$$

Introduce the operators of the transitions to the neighbor level

$$-D_{n+1} = (\frac{\partial}{\partial\upsilon} - \frac{\upsilon}{2})D_n \quad , \tag{3.2.42}$$

$$(\frac{\partial}{\partial \upsilon} + \frac{\upsilon}{2})D_n = nD_{n-1} \quad . \tag{3.2.43}$$

The dependence of the additional operator on υ can be presented as the superposition of the operators of the increase b^+ and of the decrease b^- of the level. The further considerations are analogous to the already considered ones. The construction of the approximation can not go out of the class of $i^n erfc(\upsilon)$. As the result one can get

$$f(\upsilon, \mu) = \sum_a \sum_n \sum_m c_{mna} i^n erfc(\upsilon) H_m(\mu_a) \quad . \tag{3.2.44}$$

* * *

The base of these constructions is the analogy between the mentioned kinetic equation and the harmonic oscilator in the quantum mechanics.

3.2.2 Strong hierarchy between the coefficients of absorption of the different components

The neighborhood of the saddle point of the free energy was the main object of investigation. Meanwhile in some cases the phase transition can take place far from the saddle point.

In this section the variable $\tilde{\upsilon}$ is the following one

$$\tilde{\upsilon} = \sum_a \upsilon_{la} \nu_a \quad . \tag{3.2.45}$$

There are many substances for which $n_{\infty i}$ have the different orders of the magnitudes. For example,

$$\frac{n_{\infty H_2O}}{n_{\infty H_2SO_4}} > 10^5$$

at the normal conditions.

Suppose $\tau_a \gg \tau_b$ and then $W_a^+ \ll W_b^+$. The components of the first group will be marked by the index "a" and the components of the second group will be marked by the index "b". At first we shall consider the situation of two components and later the generalization will be given.

Extract the conditions when the flow is parallel to ν_b. The quantity of the embryos in the critical region can be estimated from above by $\Delta\nu n_0 \exp(-F_c + 1)$ where $\Delta\nu$ is the halfwidht of the critical region. The normalizing factor n_0 in some situations of the overcoming of the few activation barriers can differ from the standard one. That's why we keep a special definition for this factor.

The quantity of the embryos in the critical region which change the number ν_a in the unit of time is $W_a^+ \Delta\nu n_0 \exp(-F_c + 1)$.

The number of the molecules which go inside the critical region and go outside it is the flow J_s. So, the necessary condition is the following

$$W_a^+ \Delta\nu n_0 \exp(-F_c + 1) \ll J_s \quad . \tag{3.2.46}$$

One can put $\Delta\nu$ as

$$\Delta\nu_b = (\frac{\partial^2 F(\nu_a, \nu_b)}{2\partial\nu_b^2})^{-1/2}|_{\nu_a=\nu_{ac}, \nu_b=\nu_{bc}} \quad , \tag{3.2.47}$$

and adopt for J_s the following expression

$$J_{sb} = W_b^+ n_0 \exp(-F_c)/\Delta\nu_b \pi^{1/2} \quad . \tag{3.2.48}$$

The inequality (3.2.46) comes to

$$W_a^+ \ll \frac{W_b^+}{\exp(1)(\Delta\nu_b)^2 \pi^{1/2}} \quad . \tag{3.2.49}$$

Practically the same condition can be obtained by the comparison of the characteristic time between the transitions of the embryo along ν_a and the time of the relaxation in the critical region

$$t^s = \frac{(\Delta\nu_b)^2}{W_b^+} \quad .$$

Extract the condition when there will be the equilibrium distribution at the level with the fixed ν_a of the precritical region without any dependence on the value of ν_b where the transition from the neighbor level occurs. When[19] (3.2.49) is violated the equilibrium distribution will be established in the whole precritical region.

It is sufficient to show for some point (ν_a, ν_b) the way to compensate the quantity of the embryos with the intensity greater than $J = n_0 \exp(-F_c) W^+/\Delta\nu\pi^{1/2}$. For J one can take the estimate from above $J = n_0 \exp(-F_c) W_b^+/\Delta\nu\pi^{1/2}$. The intensity of the motion of the embryos along ν_b in the boundary point is $n_0 \exp(-F_c+1) W_b^+$ and increases with the decrease of ν_b. At the band ν_a there is the quasi equilibrium distribution

$$n = n^q = n_0^q \exp(-F(\nu_a, \nu_b))|_{\nu_a=const} \quad . \tag{3.2.50}$$

[19] At $W_a^+ < W_b^+$.

The normalizing factor n_0^q differs from the standard normalizing factor because there is an equilibrium along the band but may be no equilibrium between bands. When (3.2.49) is violated the equilibrium is establish also in the number of the molecules of the other component. To establish the equilibrium it is sufficient to have the intensity of the contact between the neighbor bands greater than the intensity of the overcoming over the activation barrier. Choose as ν_b the value of ν_{be}, corresponding to the minimum of the free energy at the band

$$\nu_{be} \ : \ min_{\nu_b} F(\nu_a, \nu_b) = F(\nu_a, \nu_b) \ . \tag{3.2.51}$$

Then the intensity of the contact can be estimated by $W_a^+ n_0 \exp(-F)$. One can use the equilibrium distribution as far as if the equilibrium is established at some band it will be established at all the bands with the ν_a which are smaller. To establish the equilibrium it is sufficient that

$$W_a^+ n_0 \exp(-F(\nu_a, \nu_b)) \gg W_b^+ n_0 \exp(-F_c)/\Delta\nu\pi^{1/2} \ . \tag{3.2.52}$$

As far as the height of the pseudiactivation barrier

$$\bar{\Delta} F = F_c - F(\nu_a, \nu_{be}) \tag{3.2.53}$$

is essential then under the violation of (3.2.49) the relation (3.2.52) will be valid.

The further considerations will analyze the situation when the mentioned relation isn't valid. Then one can due to (3.2.49) assume that the transition to the post critical region occurs along ν_b, i.e. inside the band[20]. Together with ν_{be} one can introduce ν_{bx} as the point inside the band where the free energy has the maximum

$$max_{\nu_b} F(\nu_a, \nu_b) = F(\nu_a, \nu_{bx}) \equiv F_x(\nu_a) \ . \tag{3.2.54}$$

Under the square approximation the transition along ν_b can not occur because this variable is the stable one. Then $\nu_{b\ x}$ can not be defined. But if the component ν_b is supersaturated over the pure plane liquid then the condensation into the pure liquid is possible and $\nu_{b\ x}$ must exist.

The transition into the super critical region can occur under the arbitrary ν_a. But the probability of such transition is very low for all ν_a when $\exp(-F_x(\nu_a))$ differs from $\exp(-F_c)$, i.e. out of the critical region. But it can be greater than the intensity to come to the next

[20]The value $\Delta\nu_b$ depends on ν_a weakly.

band. The intensity of the establishing of the equilibrium (not the quasi equilibrium) at the next band[21] is less than the intensity of the transition to the post critical region. This intensity is given by

$$J = J_s = n_0^q \exp(-F_x(\nu_a))W_{bx}^+/\Delta_x\nu_b\pi^2 \quad , \tag{3.2.55}$$

where

$$W_{bx}^+ = W_b^+(\nu_a, \nu_{bx}); \qquad \Delta_x\nu_b = (\frac{\partial^2 F(\nu_a, \nu_b)}{2\partial\nu_b^2})^{-1/2}|_{\nu_b=\nu_{bx}} \quad . \tag{3.2.56}$$

There is no need to establish the equilibrium along the whole band with the small ν_a. The value of ν_{bx} for small ν_a is very big, the barriers of the nucleation are very high, but it is necessary to have the equilibrium only near the bottom, i.e. at ν_b near to ν_{be}. The establishing of the equilibrium along the whole precritical region of the band is necessary only for the bands where the intensity of the transition to the post critical region is essential (comparable with the intensity of the transition between the bands). According to the previous considerations there is the quasi equilibrium along such bands.

Introduce

$$N(\nu_a) = n_0^q \exp(-F(\nu_a, \nu_{b\ e}))\Delta_e\nu_b \quad , \tag{3.2.57}$$

where

$$\Delta_e\nu_b = \int_0^{\nu_{bx}} \exp(-F(\nu_a, \nu_b) + F(\nu_a, \nu_{be}))d\nu_b \quad . \tag{3.2.58}$$

At the ends of the interval of integration the equilibrium distribution can be violated but there the subintegral function goes to zero. As far as $\exp(-F)$ as function of ν_b is rather sharp near the maximum then the number of the embryos going from the band with ν_a to the band with $\nu_a - 1$ can be approximated by $W_a^-(\nu_a, \nu_{be})N(\nu_a)$. The number of the back transitions is $W_a^+(\nu_a - 1, \nu_{be})N(\nu_a - 1)$. Then one can write the balance equation at the band

$$\frac{\partial N}{\partial t} = W_a^+(\nu_a - 1, \nu_{be})N(\nu_a - 1) + W_a^-(\nu_a + 1, \nu_{be})N(\nu_a + 1) - \tag{3.2.59}$$
$$W_a^+(\nu_a, \nu_{be})N(\nu_a) - W_a^-(\nu_a, \nu_{be})N(\nu_a) - J(\nu_a) \quad .$$

[21] The intensity of transition to the next band.

For $J(\nu_a)$ one can get

$$J(\nu_a) = N\frac{W^+_{bx}\exp(F(\nu_a,\nu_{be}) - F_x(\nu_a))}{\Delta_e\nu_b\Delta_x\nu_b} \quad . \tag{3.2.60}$$

Consider the stationary solution. The last equations forms the system of algebraic equations. Note that the sufficient equations are those where $W^+_a N$ has the order of J. The equations with $W^+_a N \gg J$ can be taken into account by the boundary condition $n = n^q = n^e$ for ν_a which is less than some ν_{amin}, where J begins to be comparable with $W^+_a N$. In the region where $W^+_a N \ll J$ the solution is rather simple

$$n \ll n^e \quad . \tag{3.2.61}$$

So, one has to investigate only few equations of the type

$$\begin{aligned} &W^+_a(\nu_a - 1,\nu_{be})N(\nu_a - 1) + W^-_a(\nu_a + 1,\nu_{be})N(\nu_a + 1) \\ &-W^+_a(\nu_a,\nu_{be})N(\nu_a 1) + W^-_a(\nu_a,\nu_{be})N(\nu_a) = J(\nu_a) \quad . \end{aligned} \tag{3.2.62}$$

The total intensity is defined as

$$J_{int} = \sum_{\nu_a=\nu_{amin}}^{\nu_{amax}} J(\nu_a) \quad , \tag{3.2.63}$$

where ν_{amax} marks the upper boundary of the equations sufficient for the consideration.

In the limit when there is only one sufficient equation[22]

$$J_{int} = W^+_a \int_0^{\nu_{bx}} n_0 \exp(-F(\nu_a,\nu_b))d\nu_b \quad . \tag{3.2.64}$$

Consider the opposite situation when among (3.2.62) there are so many equations that it is difficult to solve the algebraic equations. Then it is reasonable to come to the differential form. The condition of the validity of the differential form coincides with the condition of the big number of the essential equations. Then

$$\begin{aligned} J(\nu_a) = &-\frac{\partial}{\partial\nu_a}\{(W^+_a(\nu_a,\nu_{be}) - W^-_a(\nu_a,\nu_{be}))N(\nu_a)\} + \\ &\frac{\partial^2}{2\partial\nu_a^2}\{(W^+_a(\nu_a,\nu_{be}) + W^-_a(\nu_a,\nu_{be}))N(\nu_a)\} \quad . \end{aligned} \tag{3.2.65}$$

[22]Having attained ν_a all embryos come automatically to the super critical region. Then it is possible to write the expression for the transition on ν_b.

With account of (3.2.60) one can get

$$N\frac{\exp(F(\nu_a,\nu_{be})-F_x(\nu_a))}{\Delta_e\nu_b\Delta_x\nu_b}W^+_{bx}=$$
$$\frac{\partial}{\partial\nu_a}\{(W^+_a(\nu_a,\nu_{be})(1-\exp(\frac{\partial F(\nu_a,\nu_{be})}{\partial\nu_a})))N(\nu_a)\}+ \qquad (3.2.66)$$
$$\frac{\partial^2}{2\partial\nu_a^2}\{(W^+_a(\nu_a,\nu_{be})(1+\exp(\frac{\partial F(\nu_a,\nu_{be})}{\partial\nu_a})))N(\nu_a)\} \quad .$$

One can use the following approximations

$$J=J_0\exp(cy) \quad , \qquad (3.2.67)$$

$$y=\nu_a-\nu_{a0} \quad , \qquad (3.2.68)$$

$$c=\frac{\partial F(\nu_a,\nu_{be})}{\partial\nu_a}|_{\nu_a=\nu_{a0}}-\frac{\partial F(\nu_a,\nu_{bx})}{\partial\nu_a}|_{\nu_a=\nu_{a0}} \quad , \qquad (3.2.69)$$

$$J_0=J(\nu_a)|_{\nu_a=\nu_{a0}} \quad . \qquad (3.2.70)$$

Then one can get

$$I\exp(cy)N=-W^+_a(1-\epsilon)\frac{dN}{dy}+W^+_a(1+\epsilon)\frac{d^2N}{2dy^2} \quad , \qquad (3.2.71)$$

where

$$I=\frac{W^+_{bx}\exp(F(\nu_{a0},\nu_{be})-F_x(\nu_{a0}))}{\Delta_e\nu_b\Delta_x\nu_b} \quad , \qquad (3.2.72)$$

$$W^+_a=W^+_a(\nu_a,\nu_{be}) \quad , \qquad (3.2.73)$$

$$\epsilon=\exp(\frac{\partial F(\nu_a,\nu_{be})}{\partial\nu_a}) \quad . \qquad (3.2.74)$$

It is supposed that ϵ depends on ν_a rather weakly. Then one can get

$$x=cx \quad , \quad N\exp(x)+A\frac{d^2N}{dx^2}+B\frac{dN}{dx}=0 \qquad (3.2.75)$$

with the known values of A, B.

After the transition to $\tilde{\psi}=\exp(x)$ one can get

$$A\tilde{\psi}^2N''+(A+B)\tilde{\psi}N'+\tilde{\psi}N=0 \qquad (3.2.76)$$

with the known solution

$$N=\tilde{\psi}^{-B/(2A)}Z_{B/A}(\frac{2}{\sqrt{A}}\tilde{\psi}^{1/2}) \quad , \qquad (3.2.77)$$

where Z_i is the cylinder function. One has to choose the solution vanishing at ∞. The known value of N allows to determine the total intensity of the embryo formation and the integral can be taken analytically.

In the multidimensional nucleation one has to consider one channel of nucleation.

For every set $\{\nu_a\}$ one can establish $J_{\{\nu_a\}}$ by the consideration of the evolution in the set $\{\nu_b\}$ by the standard methods from the previous sections.

After the calculation of $J_{\{\nu_a\}}$ one can define the direction. It will be the quasi integral on ν_a. This defines the first coordinate. The second coordinate is the direction of the bottom. The further consideration is absolutely analogous.

3.2.3 Small concentration in the critical embryo

Earlier we used the estimate $\xi_i \simeq 1 - \xi_i \simeq 1$. If there is $\xi_a \ll 1$ for some component then the free energy F as the function of ξ has a specific form.

Determine the form of the critical region. Denote by the index "a" the components with the small concentration and denote by the index "b" the components with the normal concentration. According to

$$\frac{\partial \xi_a}{\partial \nu_a} = \frac{1-\xi_a}{\sum_i \nu_i} \quad , \quad \frac{\partial \xi_a}{\partial \nu_{b\neq a}} = \frac{-\xi_a}{\sum_i \nu_i} \quad , \tag{3.2.78}$$

one can come to

$$\mu_i = \sum_a \frac{\partial \xi_i}{\partial \nu_a}|_c (\nu_a - \nu_{ac}) \quad , \quad \xi_i \ll 1 \quad , \tag{3.2.79}$$

Then for the fixed ξ with account of $\{v_{la}\} \simeq \{v_{lb}\}$ the variable v with some renormalization can be determined by

$$v = \sum_b \frac{\partial \kappa}{\partial \nu_b}|_c (\nu_b - \nu_{bc}) + const \quad , \quad \xi_a \ll 1 \quad , \tag{3.2.80}$$

On the base of the two last equations one can get

$$\Delta \xi_i \sim \sum_a \frac{\partial \xi_i}{\partial \nu_a}|_c \Delta \nu_a \quad , \quad \Delta v \sim \sum_b \frac{\partial \kappa}{\partial \nu_b}|_c \Delta \nu_b \quad , \quad \xi_a \ll 1 \quad , \tag{3.2.81}$$

where $\Delta \nu_a$ is the halfwidht of the critical region along ν_a.

Then the critical region is stretched along ν_b. The other variable is the rapid one. Having determined the relaxation times

$$t_{ri} = \frac{(\Delta\nu_i)^2}{W_i^+} \tag{3.2.82}$$

along the corresponding variables in the near critical region one can get (in the absence of the rapid coefficient of adsorption)

$$t_{ra} \ll t_{rb} \quad , \quad \xi_a \ll 1 \quad . \tag{3.2.83}$$

If $W_a^+ \gg W_b^+$ at $\xi_a \ll 1$ then these estimates will be even more strong. The opposite situation will be considered later.

Consider γ and v as the smooth values even for the small ξ. Then the main object is

$$b(\xi) = \sum_i \xi_i b_i(\xi) \quad , \tag{3.2.84}$$

where $b_i(\xi)$ is the excess of the chemical potential. As far as we are going to get the form of F in the critical region in a rather approximate way we can fulfill some simplifications.

One can get for $\partial b(\xi)/\partial\xi_a$ the following equation

$$\frac{\partial b(\xi)}{\partial \xi_a} = -\ln(\xi_a) + \frac{\partial b}{\partial \xi_a}|_{cont} \quad , \tag{3.2.85}$$

where $\frac{db}{d\xi}|_{cont}$ is the regular part of the derivative. It will be considered as the constant. After the integration one can come to

$$b(\xi_a) = -\xi_a \ln(\xi_a) + \xi_a(1 + \frac{\partial b}{\partial \xi_a}|_{cont}) + const \quad . \tag{3.2.86}$$

Surface excesses

One has to reconsider the definition of b

$$b(\xi) = \sum_i (\xi_i + \frac{\tilde{\nu}_i}{\sum_j \nu_j + \tilde{\nu}_j}) b_i(\xi) \quad .$$

In the surface layer there is the excess $\bar{\nu}_a$ of the rare component.

Then the most singular term in the behavior of $b(\xi)$ at the small ξ is the following

$$b \sim -\bar{\nu}_a \ln(\xi_a f_a(0))/\nu_b + const \quad , \quad \xi_a \ll 1 \quad . \tag{3.2.87}$$

Then

$$\frac{\partial b}{\partial \xi_a}|_{\xi_a=0} = \frac{\bar{\nu}_a}{\nu_b \xi_a} + \frac{\partial b}{\partial \xi_a}|_{cont} \quad , \tag{3.2.88}$$

where the second term includes all the less singular terms. After the integration[23] one can get for small ξ

$$b(\xi \approx 0) \approx \bar{\nu}_a \frac{\ln(\xi_a)}{\nu_b} + \xi_a \frac{\partial b}{\partial \xi_a}|_{cont} + const \quad . \tag{3.2.89}$$

For the equilibrium distribution n^e as the function of ξ_a at the small ξ_a it follows

$$n^e \simeq \exp(\alpha \ln \xi_a + \beta \xi_a) \quad . \tag{3.2.90}$$

In the last relation the constants α and β are known. In the case of the few rare components we have the product of such functions with the reconsideration of the normalizing factor.

The last expression is some approximation. The last approximation leads to the singular behavior of the surface tension which is in the contradiction with the Gibbs-Duhem equation

$$\sum_i \nu_i db_i - S d\gamma = 0 \quad . \tag{3.2.91}$$

But (3.2.90) is rather useful for description of the behavior of the free energy when $\xi_a \ll 1$.

As for the singularity at the zero concentration one can see according to

$$\frac{dF}{d\xi_i}|_{\xi_i=0} = -\infty \quad , \quad \frac{dF}{d\xi_i}|_{\xi_i=1} = \infty \tag{3.2.92}$$

that $\xi_i = 0$ isn't profitable energetically. So, the error of the approximation occurs in the negligible point.

In the natural approximation of a hard wall one can come from ξ to $\xi - \xi_0$ where ξ_0 is the equilibrium value of ξ and use the approximation

$$n^e \simeq \exp(-\beta \xi_a) \quad , \quad \xi_a > 0 \quad , \quad n^e \simeq \infty \quad , \quad \xi_a < 0 \quad , \tag{3.2.93}$$

corresponding to (3.2.90) with $\alpha = 0$.

Separation of the variables.

One has to extract the main operator corresponding to (3.2.90) or (3.2.93).

[23]The more precise equation is $n^e \simeq \exp(\alpha \ln \xi_a + \beta \xi_a + \gamma \xi_a \ln \xi_a)$.

The Lorenz transformation can not be applied here. It seems that the great number of the cross terms will appears. But at the small concentrations the concentration of the component has practically the same direction as the number of the molecules of the given component.

The initial variables ν_a practically coincide with the direction of κ, ξ_i for the rare components. So, there occurs the approximate separation of the variables for all rare components.

Inside the group of the components with the normal concentration the variables can be separated by the internal Lorenz transformation.

The variable ξ_a is the rapid one. Having used as the approximation (3.2.90) one can get

$$\frac{\partial n}{\partial t} = \Lambda_\xi n + A_\xi n \quad , \quad A_\xi = L - \Lambda_\xi \quad , \tag{3.2.94}$$

$$\Lambda_\xi = \sum_a \Lambda_{\xi_a} \quad ,$$

$$\Lambda_{\xi_a} n = \frac{\partial}{\partial \xi_a} n^e \frac{\partial}{\partial \xi_a} f \quad , \quad f = \frac{n}{n^e} \quad . \tag{3.2.95}$$

The variables are separated also in the boundary conditions $f = 1$ at $\nu_a \sim \nu_{ac} - \Delta\nu_a$, $f = 0$ at $\nu_a \sim \nu_{ac} + \Delta\nu_a$.

Eigenfunctions and eigenvalues

Find the eigenfunctions of Λ_{ξ_a}. One can also find the eigenfunction corresponding to the zero eigenvalue and determine the actions of the superposition of the operators of the multiplication and differentiation on this function.

Note that A_ξ consists from the superpositions of the products of ξ_a and the derivatives on ξ_a for the different a. Taking into account $n = n^e f = \Pi_a \xi_a^\alpha \exp(-\xi_a) f$ one can see[24]

$$\xi n = \xi^{\alpha+1} \exp(-\xi) f \quad , \tag{3.2.96}$$

$$\frac{\partial n}{\partial \xi} = \alpha \xi^{\alpha-1} \exp(-\xi) f - \xi^\alpha \exp(-\xi) f + \xi^\alpha \exp(-\xi) \frac{\partial f}{\partial \xi}$$

(index a is omitted). It is easy to construct on the base of A_ξ the operator

$$A_\xi n = n^e \hat{A}_\xi f \quad . \tag{3.2.97}$$

[24]The rescaling of the concentration can lead to $\beta = 1$.

Operator $\hat{A}_\xi$ consists of the superposition of the derivatives on ξ_a and products of ξ_a. Instead of (3.2.94) one can get

$$\frac{\partial f}{\partial t} = \hat{\Lambda}_\xi f + n^e \hat{A}_\xi f \quad , \tag{3.2.98}$$

$$\Lambda_{\xi_a} n = n^e \hat{\Lambda}_{\xi_a} f \quad , \quad \hat{\Lambda}_\xi = \sum_a \hat{\Lambda}_{\xi_a} \quad .$$

Operator $\hat{\Lambda}_{\xi_a}$ can be rewritten as

$$\hat{\Lambda}_{\xi_a} f = \frac{\partial}{\partial \xi_a}[\xi_a^\alpha \exp(\xi_a)\frac{\partial}{\partial \xi_a} f] = \xi_a^\alpha \exp(\xi_a)[(\frac{\alpha}{\xi_a} + 1)\frac{\partial}{\partial \xi_a} f + \frac{\partial^2}{\partial \xi_a^2} f] \quad . \tag{3.2.99}$$

Then (3.2.98) can be rewritten as

$$\frac{\partial f}{\partial t} = \sum_a \hat{\Lambda}_{\xi_a} f + \hat{A}_\xi f \quad , \quad \hat{\Lambda}_{\xi_a} = \frac{\alpha + \xi_a}{\xi_a}\frac{\partial}{\partial \xi} + \frac{\partial^2}{\partial \xi^2} \quad . \tag{3.2.100}$$

The eigenfunctions are the Lagerr polynomials

$$L_n^\alpha = \frac{1}{n!}\exp(\xi_a)\xi_a^{-\alpha}\frac{d^n}{d\xi_a^n}\exp(\xi_a)\xi_a^{n+\alpha} \quad , \tag{3.2.101}$$

which correspond to the eigenvalues

$$\lambda_n = -n \quad . \tag{3.2.102}$$

Lagerr polynomials form the complete basis with the weight $\exp(-\xi + \alpha \ln(\xi))$ at $[0, \infty]$. The real interval for the concentration $[0, \beta]$ is finite, but one can not practically attain the essential values of the concentration[25].

One has to restrict the decomposition by the number of the polynomial which has the scale of localization comparable with the normal concentration.

Introduce the scalar product

$$< \varphi, \hat{\psi} >= \int_0^\infty \varphi\hat{\psi}\exp(-\xi_a)\xi_a^\alpha d\xi_a \quad , \tag{3.2.103}$$

and get

$$< L_n^\alpha, L_m^\alpha >= \delta_{mn}\frac{\Gamma(\alpha + n + 1)}{n!} \quad . \tag{3.2.104}$$

[25]In the opposite situation there is no channel as an object.

Lagerr polynomials have the following properties

$$\frac{d}{d\xi_a}L_n^\alpha = -L_{n-1}^{\alpha+1} \quad , \tag{3.2.105}$$

$$L_n^{\alpha+1} = \sum_{m=0}^{n} L_m^\alpha \quad . \tag{3.2.106}$$

So, the differentiation $d/d\xi_a$ can be presented as the superposition of the operators a^- of the decrease of the level. The multiplication on ξ according to

$$\xi_a L_n^\alpha(\xi_a) = -(n+1)L_{n+1}^\alpha(\xi_a) + (2n+\alpha+1)L_n^\alpha(\xi_a) - (n+\alpha)L_{n-1}^\alpha(\xi_a) \tag{3.2.107}$$

can be presented as the superposition of the operators a^+ of the increase of the level and the operators a^- of the increase of the level.

The further construction are absolutely analogous to the square case.

If one applies (3.2.93) then the main operator is

$$\Lambda_\xi n = \frac{\partial}{\partial\xi}\exp(-\xi)\frac{\partial}{\partial\xi}f = \exp(-\xi)[-\frac{\partial}{\partial\xi}f + \frac{\partial^2}{\partial\xi^2}f] \quad . \tag{3.2.108}$$

After the introduction of $\hat{\Lambda}_\xi$ one can see that

$$\hat{\Lambda}_\xi f = [-\frac{\partial}{\partial\xi} + \frac{\partial^2}{\partial\xi^2}]f \quad . \tag{3.2.109}$$

Then $\hat{\Lambda}_\xi$ can be inverted by the Laplace transformation.

Some consequences

In the case of the of the strong hierarchy between the coefficients of the adsorption it is possible to have the rapid component not across the channel but along the channel. Then the condensation is effectively the one dimensional one. But the variables can be separated and there is no need in the hierarchy of the establishing of the equilibrium. The solution can be, thus, constructed in this case also. The separation of the variables takes place also in the boundary conditions.

In the considerations of the first chapter we assume that the concentration is the normal one. Now we see that when the concentration is small we can not use the square approximation.

Only under the small concentration it is possible that the variation of the absorption coefficient radically changes the picture of the condensation.

* * *

Due to the result of the constructions of this chapter the role of the Lorenz transformation in the theory of nucleation isn't so impressive as it can be predicted from the first point of view. The flow can be changed essentially from the trivial consideration along the steepens descent line only under the hierarchy of the kinetic coefficients. But this very situation leads to the redefinition of the near critical region (where the Lorenz transformation can not be applied) or at least allows more simple description. The only case where this hierarchy doesn't lead to the reconsideration of the position of the near critical region is th e situation with the low concentration. But here also the Lorenz transformation can not be applied.

3.3 Squeeze description

3.3.1 Multidimensional kinetic equation

The connection between $n(\xi, \kappa)$ and $n(\{\nu_a\})$ is given by

$$n(\xi,\kappa) = n(\{\nu_a\})\ det \left\| \begin{array}{ccccc} \frac{\partial \nu_a}{\partial \kappa} & \frac{\partial \nu_a}{\partial \xi_1} & \frac{\partial \nu_a}{\partial \xi_2} & ... & \frac{\partial \nu_a}{\partial \xi_{m-1}} \\ ... & ... & ... & ... & ... \\ \frac{\partial \nu_b}{\partial \kappa} & \frac{\partial \nu_b}{\partial \xi_1} & \frac{\partial \nu_b}{\partial \xi_2} & ... & \frac{\partial \nu_b}{\partial \xi_{m-1}} \\ ... & ... & ... & ... & ... \end{array} \right\| \quad . \quad (3.3.1)$$

After the transition to ξ, κ one can get the following form of the kinetic equation

$$\frac{\partial\ n}{\partial\ t} = -\sum_i [\delta_i\kappa \frac{\partial}{\partial\kappa} + \sum_a \delta_i\xi_a \frac{\partial}{\partial\xi_a}] J_i \quad , \quad (3.3.2)$$

$$J_i = W_i^+[n(\kappa,\{\xi\}) - (\delta_i\kappa\frac{\partial}{\partial\kappa} + \sum_a \delta_i\xi_a \frac{\partial}{\partial\xi_a})n(\kappa,\{\xi\})] - W_i^-(\kappa,\{\xi\})n(\kappa,\{\xi\}) \ .$$

Here $\delta_i\xi_a$ and $\delta_i\kappa$ are the elementary variations in the elementary acts of the absorption and the ejection of the molecules $\delta_i\kappa = \frac{\partial\kappa}{\partial\nu_i}$, $\delta_i\xi_a = \frac{\partial\xi_a}{\partial\nu_i}$.

The sums over the the concentrations ξ_i have to be carried out from $i = 1$ till $m - 1$. It will will be omitted later.

The last equation can be obtained from the form of the finite differences

$$\frac{\partial\ n}{\partial\ t} = \sum_i [n(\kappa - \delta_i\kappa, \{\xi - \delta_i\xi\})W_i^+(\kappa - \delta_i\kappa, \{\xi - \delta_i\xi\}) -$$

$$n(\kappa,\xi)W_i^+(\kappa,\xi) + n(\kappa+\delta_i\kappa,\{\xi+\delta_i\xi\}) \quad (3.3.3)$$
$$W_i^-(\kappa+\delta_i\kappa,\{\xi+\delta_i\xi\}) - n(\kappa,\xi)W_i^-(\kappa,\xi)] \quad .$$

Suppose that the asymptotes $\mid \partial B(\xi)/\partial\xi_a \mid \to \infty$ at $\xi_a \to 0$; $\xi_a \to 1$ ensure $\xi_a \sim 1-\xi_a$. Then the application of $\partial/\partial\xi_a$ to n gives

$$\frac{\partial n}{\partial \xi_a} \sim -(\frac{\partial^2 F}{\partial \xi_a^2})^{1/2} n \sim \kappa^{1/2}(\frac{\partial^2 B(\xi)}{\partial \xi_a^2})^{1/2} n \quad , \qquad (3.3.4)$$

and the second derivative is taken at the saddle point. The last equation is obtained of the base of the equilibrium distribution instead of n.

Apply the operator $\partial/\partial\xi$ to the function constructed on the base of the solution of the relaxation equation. This equation can be written in the following form

$$\frac{\partial \xi_a}{\partial t} = \kappa^{-1/3} L(\xi)(\xi_a - \xi_{a\,+}) \quad , \qquad (3.3.5)$$

where L is some known function of ξ and $\xi_{a\,+}$ is the stationary value of ξ_a.

The law of the growth of ξ is

$$\frac{\partial \xi_a}{\partial t} \sim (W^+ - W^-)\delta\xi_a \quad , \qquad (3.3.6)$$

where W^+ and W^- are the characteristic values for the direct and inverse flows and $\delta\xi_a$ is the characteristic variation of ξ in the elementary act.

Taking into account

$$W^- = W^+ \exp(\frac{\partial^2 F}{\partial \xi_a^2} \mid_{\xi_a=\xi_{a\,+}} \delta\xi_a(\xi_a - \xi_{a\,+})) \sim \qquad (3.3.7)$$
$$W^+(1 + \frac{\partial^2 F}{\partial \xi_a^2} \mid_{\xi_a=\xi_{a\,+}} \delta\xi_a(\xi_a - \xi_{a\,+})) \quad ,$$

one can come to

$$\kappa^{-1/3} L(\xi) \sim const \frac{\partial^2 F}{\partial \xi_a^2} \mid_{\xi_a=\xi_{a\,+}} \sim -\kappa \frac{\partial^2 B}{\partial \xi_a^2} \mid_{\xi_a=\xi_{a\,+}} \quad . \qquad (3.3.8)$$

Characteristic values of terms in kinetic equation

The evolution equation can be rewritten as

$$\frac{\partial\ n}{\partial\ t} = -\sum_a \frac{\partial n K_{\xi_a}}{\partial \xi_a} - \frac{\partial n K_\kappa}{\partial \kappa} + \sum_a \sum_b \frac{\partial^2 n K_{\xi_a \xi_b}}{\partial \xi_a \partial \xi_b} + \sum_a \frac{\partial^2 n K_{\kappa \xi_a}}{\partial \xi_a \partial \kappa} + \frac{\partial^2 n K_{\kappa\kappa}}{\partial \kappa^2} \quad , \tag{3.3.9}$$

where

$$K_{\xi_a} = \sum_i \delta_i \xi_a (W_i^+ - W_i^-) \quad , \tag{3.3.10}$$

$$K_\kappa = \sum_i \delta_i \kappa (W_i^+ - W_i^-) \quad , \tag{3.3.11}$$

$$K_{\xi_a \xi_b} = \frac{1}{2} \sum_i \delta_i \xi_a \delta_i \xi_b (W_i^+ + W_i^-) \quad , \tag{3.3.12}$$

$$K_{\kappa\kappa} = \frac{1}{2} \sum_i \delta_i^2 \kappa (W_i^+ + W_i^-) \quad , \tag{3.3.13}$$

$$K_{\kappa \xi_a} = \sum_i \delta_i \xi_a \delta_i \kappa (W_i^+ + W_i^-) \quad . \tag{3.3.14}$$

Taking into account that

$$\delta_i \xi_a = \frac{\partial \xi_a}{\partial \nu_i} \quad , \qquad \delta_i \kappa = \frac{\partial \kappa}{\partial \nu_i} \quad ,$$

one can come to

$$K_{\xi_a} = \sum_b \frac{\partial \xi_a}{\partial \nu_b} (W_b^+ - W_b^-) = \frac{\partial\ \xi_a}{\partial\ t} \quad , \quad K_\kappa = \sum_b \frac{\partial \kappa}{\partial \nu_b} (W_b^+ - W_b^-) = \frac{\partial\ \kappa}{\partial\ t} \quad . \tag{3.3.15}$$

One can get the following estimates

$$\delta_a \kappa \sim v_{l\ a} \quad , \qquad \delta_a \xi \sim \kappa^{-1} \quad . \tag{3.3.16}$$

Suppose that all W_a^+ have one and the same characteristic values ($\sim \kappa^{2/3}$), then in the post critical region[26]:

$$K_{\xi_a} \sim W_i^+ \frac{\xi_a - \xi_{a\ +}}{\kappa} \quad , \qquad K_\kappa \sim W_i^+ \quad , \qquad K_{\xi_a \xi_b} \sim \frac{W_i^+}{\kappa^2} \quad , \qquad K_{\kappa\kappa} \sim W_i^+ \quad , \qquad K_{\xi_a \kappa} \sim \frac{W_i^+}{\kappa} \quad . \tag{3.3.17}$$

[26] After rescaling $\delta_a \kappa \sim 1$.

All coefficients except K_{ξ_a} conserve the power of ξ_a.
For the r.h.s. of (3.3.9) one can come to

$$| \frac{\partial n K_{\xi_a}}{\partial \xi} | \sim | \frac{n W_i^+ (\xi_a - \xi_{a\,+})}{\kappa \Delta \xi_a} + \frac{n W_i^+}{\kappa} + \frac{n W_i^+}{\kappa} \frac{\partial L}{\partial \xi_a} (\xi_a - \xi_{a+}) | \tag{3.3.18}$$

$$, \quad | \frac{\partial n K_\kappa}{\partial \kappa} | \sim | \frac{n W_i^+}{\kappa} | \ ,$$

$$| \frac{\partial^2 n K_{\xi_a \xi_b}}{\partial \xi_a \partial \xi_b} | \leq | \frac{W_i^+}{\kappa^2} \frac{n}{\Delta \xi_a \Delta \xi_b} + \frac{n W_i^+}{(\Delta \xi_a) \kappa^2} | \ , \tag{3.3.19}$$

$$| \frac{\partial^2 n K_{\kappa\kappa}}{\partial \kappa^2} | \leq | \frac{n W_i^+}{\kappa^2} | \ , \quad | \frac{\partial^2 n K_{\kappa \xi_a}}{\partial \kappa \partial \xi_a} | \leq | \frac{n W_i^+}{\kappa^2 \Delta \xi_a} | \ , \tag{3.3.20}$$

where $\Delta \xi_a$ is the halfwidht of the distribution along ξ_a.

It is necessary to estimate the action of $\partial / \partial \kappa$ on n. In the stationary situation it is reasonable to put the intensity of the embryos formation equal to J. Due to the regular growth of κ one can get

$$\frac{\partial\, n}{\partial \kappa} \sim \frac{\partial}{\partial \kappa} (\frac{J}{d\kappa / dt}) \sim \frac{J}{\kappa d\kappa / dt} \sim \frac{n}{\kappa} \ . \tag{3.3.21}$$

Analyze the action of the different terms of (3.3.9):

$$\frac{| \frac{\partial}{\partial \xi_a} n K_{\xi_a} |}{W_i^+ n} \equiv A \sim \frac{\xi_a - \xi_{a\,+}}{\kappa\ \Delta \xi_a} + \kappa^{-1} + \frac{\xi - \xi_{a+}}{\kappa} \frac{\partial L}{\partial \xi_a} \ , \tag{3.3.22}$$

$$\frac{| \frac{\partial}{\partial \kappa} n K_\kappa |}{W_i^+ n} \equiv B \sim \kappa^{-1} \ ,$$

$$\frac{| \frac{\partial^2}{\partial \xi_a \partial \xi_b} n K_{\xi_a \xi_b} |}{W_i^+ n} \equiv C \leq \kappa^{-2} (\Delta \xi_a)^{-1} (\Delta \xi_b)^{-1} + \kappa^{-2} (\Delta \xi_a)^{-1} \ , \tag{3.3.23}$$

$$\frac{| \frac{\partial^2}{\partial \kappa^2} n K_{\kappa\kappa} |}{W_i^+ n} \equiv D \sim \kappa^{-2} \ , \quad \frac{| \frac{\partial^2}{\partial \kappa \partial \xi_a} n K_{\kappa \xi_a} |}{W_i^+ n} \equiv E \sim \kappa^{-2} (\Delta \xi_a)^{-1} \ . \tag{3.3.24}$$

The value $\Delta \xi$ has the sense of the halfwidht of the distribution along ξ. It is necessary to consider ξ for which

$$\xi - \xi_+ \leq \Delta \xi \ . \tag{3.3.25}$$

Due to $\frac{\partial L}{\partial \xi_a} \sim 1$ ($\Delta\xi_a \leq 1$ the last part of the first term can be omitted.

When

$$\xi - \xi_+ \sim \Delta\xi \tag{3.3.26}$$

then the first and the second terms have the same order. The value of the forth term is negligible.

Suppose that the fifth term and the first part of the third term have the same order. Then $\Delta\xi \sim 1$ and

$$A \sim \kappa^{-1}(\xi - \xi_+) + \kappa^{-1} \ , \quad B \sim \kappa^{-1} \ , \quad C \sim \kappa^{-2} \ , \quad E \sim \kappa^{-2} \ . \tag{3.3.27}$$

Then the third and the fifth terms are negligible in comparison with the second term.

When $\Delta\xi$ decreases and attains $\Delta\xi \sim \kappa^{-1/2}$, then $B \sim \kappa^{-1}$, $C \sim \kappa^{-1}$, $E \sim \kappa^{-3/2}$.

Suppose that the fifth term has the order of the second term. Then $\Delta\xi \sim \kappa^{-1}$ which leads to

$$B \sim \kappa^{-1} \ , \quad C \sim 1 \ , \quad E \sim \kappa^{-1} \ . \tag{3.3.28}$$

When $\Delta\xi$ becomes more small then the last estimate remains valid. So, the fifth term can be neglected. It is very small because $\Delta\xi > 1/\kappa$ at $E < B$ and when $\Delta\xi < 1$ then E is less than the first part of the third term. The possibility to neglect the higher derivatives and the possibility to use the Fokker-Planck approximation can be shown analogously.

* * *

The first term leads to the convergence along the intensive variable. If the third term isn't essential then $\Delta\xi$ decreases until the third term will have the same order as the first one. If the distribution function is narrow and the action of the first term is rather weak then the diffusion leads to the increase of the width until the first term will compensate the diffusion. So, the first term has the same power as the third term has. It leads to the following estimate

$$\Delta\xi \sim \kappa^{-1/2} \ . \tag{3.3.29}$$

From the last equation it follows that the spectrum is rather narrow along ξ. Then it is possible to put ξ to ξ_+. Then

$$\frac{d\kappa}{dt} = const(\xi_+)\kappa^{2/3} \ . \tag{3.3.30}$$

After the integration one can come to

$$\kappa \approx const \;\; t^3 \;\; . \tag{3.3.31}$$

* * *

Introduce the variables $\nu_=$ and $\nu_\perp$ which can be gotten from $\{\nu_a\}$ by the rotation, $\nu_=$ is parallel to κ. The order of the elements of the kinetic matrix is W_i^+. The halfwidht along $\nu_\perp$ can be estimated as

$$\Delta\nu_\perp \sim \nu_=^{1/2} \;\; . \tag{3.3.32}$$

From (3.3.30) one can get the estimate for the halfwidht of the equilibrium distribution moving along κ

$$\Delta\nu_\perp \sim t^{3/2} const \;\; . \tag{3.3.33}$$

For the Green function of the diffusion equation along $x \sim \nu_\perp$ with the absence of the regular growth one can get the following expression

$$G(x_0, 0; x, t) \sim \frac{\exp(-\frac{(x-x_0)^2}{4Dt})}{t^{(m-1)/2} D^{(m-1)/2}} \;\; , \tag{3.3.34}$$

where D is the diffusion coefficient ($D \sim W_a^+$), m is the dimension of the space. The front of the distribution is moving with the velocity less than

$$\frac{d\Delta x}{dt} \sim D^{1/2} t^{1/2} \;\; . \tag{3.3.35}$$

After some moment this velocity is less than the velocity of the increase of $\Delta\nu_\perp$. Later the accuracy of the approximation increases and one can neglect the relaxation (which can be seen at $\nu_\perp - \nu_{\perp\,+} \sim \Delta\nu_\perp \sim t^{3/2}$). At the same time $\nu_\perp$ approaches to the stationary value $\nu_{\perp\,+}$. The distribution function after some κ can be presented in the following form

$$n(\nu_=, \nu_\perp) = n_{\nu_=}(\nu_=) n_{\nu_\perp}(\nu_\perp) \tag{3.3.36}$$

The function $n_{\nu_\perp}(\nu_\perp)$ can be determined by the diffusion equation

$$\frac{\partial n_{\nu_\perp}}{\partial t} = \sum_a D_a \frac{\partial^2 n_{\nu_\perp}}{\partial \nu_{\perp\,a}^2} \;\; , \tag{3.3.37}$$

where D_a are the corresponding coefficients of diffusion in the coordinates $\nu_{\perp\,a}$ on the hyperplane $\nu_\perp$. The solution of this equation resembles

after some moment (or some size κ) the Green function of the diffusion equation

$$G \sim \Theta(t) \frac{\exp(-\frac{\sum_a (\nu_{\perp\ a} - \nu_{\perp\ \ a\ +})^2}{4D_a t})}{t^{(m-1)/2}} \quad . \tag{3.3.38}$$

The function $n_{\nu_=}$ can be obtained from the law of the regular growth and with the help of (3.3.31) in the following form

$$n_{\nu_=}(\nu_=) = \frac{J_s(t_{\nu_=})}{d\nu_=/dt} \quad , \tag{3.3.39}$$

where J_s is the intensity of the formation of the post critical embryos and $t_{\nu_=}$ is the moment when the embryo appears in the super critical region.

* * *

The stationary distribution can be obtained by the solution of the following equation

$$\frac{\partial n}{\partial t} \sim \frac{\partial n}{\partial \rho} \sim D \frac{\partial^2 n}{\partial \nu_\perp^2} \quad , \tag{3.3.40}$$

where $\rho = \nu_=^{1/3}$. Taking into account that

$$D \sim \nu_=^{2/3} = \rho^2 \quad , \tag{3.3.41}$$

one can obtain the diffusion equation

$$\frac{\partial n}{\partial \nu_=} \sim const \frac{\partial^2 n}{\partial \nu_\perp^2} \tag{3.3.42}$$

with the δ-like source at $\kappa = 0$ and $\xi = \xi_+$. The solution of this equation is given by the Green function.

* * *

More precise solution can be obtained after the introduction in the diffusion equation of the terms corresponding to the regularly growth. After the linearization of these terms on $\xi - \xi_+$ one can get the analogous equation which can be solved with the help of the Green function. The initial condition must be the δ-like source at $\kappa = 0$ and $\xi = \xi_c$, This equation can be rewritten in the following form

$$\frac{\partial P}{\partial t} = \gamma \frac{\partial}{\partial x}(xP) + D \frac{\partial^2}{\partial x^2} P \tag{3.3.43}$$

with the known constants γ and D, where P is the Green function with the expression

$$P(x,t|x',t') = \sqrt{\frac{\gamma}{2\pi D(1-\exp(-2\gamma(t-t'))}}\exp(-\frac{\gamma(x-\exp(-\gamma(t-t'))x')^2}{2D(1-\exp(-2\gamma(t-t')))}) \quad . \tag{3.3.44}$$

The variable x has the sense of the deviation of $\nu_\perp$ from the stationary value $\nu_{\perp+}$.

3.3.2 Hierarchy in the critical region

The time $t_{\nu_\perp}$ of the relaxation along the stable variable $\nu_\perp$ is estimated (all variables for every component have the same order) by

$$t_{\nu_\perp} \sim \frac{\Delta^2\nu_\perp}{W_i^+} \quad . \tag{3.3.45}$$

The time of the overcoming of the critical region can be estimated by

$$t_{\nu_=} \sim \frac{\Delta^2\nu_=}{W_i^+} \quad . \tag{3.3.46}$$

Take into account

$$\frac{\partial^2 F}{\partial\kappa^2} = \frac{-2\kappa^{-4/3}}{9} \quad , \quad \frac{\partial^2 F}{\partial\xi_a\partial\xi_b} = -\kappa\frac{\partial^2 B(\xi)}{\partial\xi_a\partial\xi_b} \quad , \quad \frac{\partial^2 F}{\partial\kappa\partial\xi_a} = 0 \quad . \tag{3.3.47}$$

One can get the following estimates for the halfwidth

$$\Delta\nu_= \sim \Delta\kappa \sim \kappa^{2/3} \quad , \quad \Delta\nu_\perp \sim \kappa\Delta\xi \sim \kappa^{1/2} \quad . \tag{3.3.48}$$

One can note that

$$\frac{t_{\nu_\perp}}{t_{\nu_=}} \sim \kappa^{-1/3} \to 0 \quad . \tag{3.3.49}$$

The last equation shows the existence of the equilibrium along $\nu_\perp$ which is translated from the precritical region to the post critical region. In the super critical region this distribution will be transformed.

Reduce the square form of the free energy to the sum of squares. The new variables are marked by the same symbols. Then the solution can be written as

$$n(\kappa,\xi) = n_\kappa(\kappa)\Pi_i n_{\xi_i}(\xi) \quad , \tag{3.3.50}$$

where

$$n_\kappa(\kappa) = \int d\xi_1 ... d\xi_{m-1} n(\kappa, \{\xi_i\}) \tag{3.3.51}$$

and

$$n_{\xi_i}(\xi) \sim \exp(-\frac{\partial^2 F}{\partial \xi_i^2} \mid_c (\xi_i - \xi_{c\ i})^2) \tag{3.3.52}$$

is the equilibrium distribution along ξ_i. The function n_κ satisfies to the one dimension equation with the known solution.

3.3.3 Relaxation of concentration of solution in embryos

Use the model of the ideal solution. The evolution equation can be written in the following manner

$$\frac{d\nu_a}{dt} = \frac{V^{2/3}}{\tau_a}[\zeta_a + 1 - \frac{\nu_a}{\sum_b \nu_b}] \ , \tag{3.3.53}$$

where

$$V = \sum_a v_{al} \nu_a \tag{3.3.54}$$

and

$$\tau_a = 4[(36\pi)^{1/3} n_{aa} v_{t\ a}]^{-1} \ . \tag{3.3.55}$$

Consider the binary system Then for

$$\hat{\xi} = \frac{\nu_a}{\nu_b} \tag{3.3.56}$$

one can get

$$\frac{d\hat{\xi}}{dt} = \frac{V^{2/3}}{\nu_b}[\frac{\zeta_a + (\hat{\xi}+1)^{-1}}{\tau_a} - \hat{\xi}\frac{\zeta_b + 1 - (\hat{\xi}+1)^{-1}}{\tau_b}] \ . \tag{3.3.57}$$

It is necessary to express ν_b via $\hat{\xi}$ and V

$$\nu_b = \frac{V}{v_{l\ a}\hat{\xi} + v_{l\ b}} \tag{3.3.58}$$

and to substitute to the relaxation equation. Then

$$\frac{d\hat{\xi}}{dt} = V^{-1/3}(v_{l\ a}\hat{\xi} + v_{l\ b})[\frac{\zeta_a + (\hat{\xi}+1)^{-1}}{\tau_a} - \hat{\xi}\frac{\zeta_b + 1 - (\hat{\xi}+1)^{-1}}{\tau_b}] \ . \tag{3.3.59}$$

Near the stationary value $\hat{\xi}_+$ of the variable $\hat{\xi}$ the last equation can be reduced to

$$\frac{d\hat{\xi}}{dt} = -V^{-1/3}(v_{l\ a}\hat{\xi_+} + v_{l\ b})\frac{(\zeta_b+1)(\hat{\xi}-\hat{\xi}_+)(\hat{\xi}_+-\hat{\xi}_-)}{\tau_b(1+\hat{\xi}_+)} \quad , \qquad (3.3.60)$$

where ξ_- is second root of the square polynomial in the denominator. The evolution of V is described by

$$\frac{dV}{dt} = V^{2/3}[\frac{v_{l\ a}}{\tau_a}(\zeta_a + \frac{1}{1+\hat{\xi}}) + \frac{v_{l\ b}}{\tau_b}(\zeta_b + 1 - \frac{1}{1+\hat{\xi}})] \quad . \qquad (3.3.61)$$

Substitute $\hat{\xi}$ in the last equation by $\hat{\xi}_+$. After the integration

$$V^{1/3} = \frac{P(\hat{\xi}_+)}{3}(t-t_0) \quad , \qquad (3.3.62)$$

where

$$P(\hat{\xi}) = [\frac{v_{l\ a}}{\tau_a}(\zeta_a + \frac{1}{1+\hat{\xi}}) + \frac{v_{l\ b}}{\tau_b}(\zeta_b + 1 - \frac{1}{1+\hat{\xi}})] \quad . \qquad (3.3.63)$$

Here t_0 is the time of the appearing of the droplet. The regular law of evolution can be prolonged[27] until the zero size.

Then

$$\frac{d\hat{\xi}}{dt} = -\frac{3}{P(\hat{\xi}_+)}(t-t_0)^{-1}G(\hat{\xi}_+)(\hat{\xi}-\hat{\xi}_+) \quad , \qquad (3.3.64)$$

where

$$G(\hat{\xi}_+) = \frac{(v_{l\ a}\hat{\xi}_+ + v_{l\ b})(1+\zeta_b)(\hat{\xi}_+-\hat{\xi}_-)}{(1+\hat{\xi}_+)\tau_b} \quad . \qquad (3.3.65)$$

After the integration one can get

$$\hat{\xi} - \hat{\xi}_+ = const(t-t_0)^{-3G(\hat{\xi}_+)/P(\hat{\xi}_+)} \quad . \qquad (3.3.66)$$

On the base of the consideration of the global evolution one can show that

$$V \gg V_c \qquad (3.3.67)$$

[27] In the context of the global theory

at the characteristic time of PIFD. With the help of the initial condition[28]

$$\hat{\xi} \mid_{V=V_c} = \hat{\xi}_c \tag{3.3.68}$$

one can get the following relaxation law

$$\frac{\hat{\xi} - \hat{\xi}_+}{\hat{\xi}_c - \hat{\xi}_+} = [\frac{V}{V_c}]^{-\hat{\gamma}} \quad , \qquad \hat{\gamma} = \frac{G(\hat{\xi}_+)}{P(\hat{\xi}_+)} \quad . \tag{3.3.69}$$

Estimate $\hat{\gamma}$ from above. From (3.3.63), (3.3.64) it follows that

$$\hat{\gamma} = \frac{(v_{l\ b} + \hat{\xi}_+ v_{l\ a})(\hat{\xi}_+ + 1)^{-1}(\zeta_b + 1)\tau_b^{-1}(\hat{\xi}_+ - \hat{\xi}_-)}{[\frac{v_{l\ a}}{\tau_a}(\zeta_a + \frac{1}{1+\hat{\xi}_+}) + \frac{v_{l\ b}}{\tau_b}(\zeta_b + 1 - \frac{1}{1+\hat{\xi}_+})]} \quad . \tag{3.3.70}$$

Due to

$$[\frac{v_{l\ a}}{\tau_a}(\zeta_a + \frac{1}{1+\hat{\xi}_+}) + \frac{v_{l\ b}}{\tau_b}(\zeta_b + 1 - \frac{1}{1+\hat{\xi}_+})] \leq [\frac{v_{l\ a}}{\tau_a}(\zeta_a + 1) + \frac{v_{l\ b}}{\tau_b}(\zeta_b + 1)] \tag{3.3.71}$$

the estimate for $\hat{\gamma}$ is the following

$$\hat{\gamma} \geq \frac{(v_{l\ b} + \hat{\xi}_+ v_{l\ a})(\hat{\xi}_+ + 1)^{-1}(\zeta_b + 1)\tau_b^{-1}(\hat{\xi}_+ - \hat{\xi}_-)}{[\frac{v_{l\ a}}{\tau_a}(\zeta_a + 1) + \frac{v_{l\ b}}{\tau_b}(\zeta_b + 1)]} \quad . \tag{3.3.72}$$

Ordinary $v_{l\ a} \approx v_{l\ b}$. Then

$$\frac{(v_{l\ b} + \hat{\xi}_+ v_{l\ a})(\hat{\xi}_+ + 1)^{-1}(\zeta_b + 1)\tau_b^{-1}(\hat{\xi}_+ - \hat{\xi}_-)}{[\frac{v_{l\ a}}{\tau_a}(\zeta_a + 1) + \frac{v_{l\ b}}{\tau_b}(\zeta_b + 1)]} \approx \frac{\frac{\zeta_b + 1}{\tau_b}(\hat{\xi}_+ - \hat{\xi}_-)}{[\frac{1}{\tau_a}(\zeta_a + 1) + \frac{1}{\tau_b}(\zeta_b + 1)]} \quad . \tag{3.3.73}$$

Taking into account

$$\hat{\xi}_+ - \hat{\xi}_- = \frac{\tau_b D}{\zeta_b + 1} \quad , \tag{3.3.74}$$

where

$$D = \sqrt{[\frac{\zeta_a}{\tau_a} - \frac{\zeta_b}{\tau_b}]^2 + 4\frac{(\zeta_a + 1)(\zeta_b + 1)}{\tau_a \tau_b}} \quad , \tag{3.3.75}$$

[28]This condition is rather approximate. It is valid in the context of the global evolution.

one can see

$$\hat{\gamma} \geq \frac{\sqrt{[\frac{\zeta_a}{\tau_a} - \frac{\zeta_b}{\tau_b}]^2 + 4\frac{(\zeta_a+1)(\zeta_b+1)}{\tau_a\tau_b}}}{[\frac{1}{\tau_a}(\zeta_a+1) + \frac{1}{\tau_b}(\zeta_b+1)]} \quad . \tag{3.3.76}$$

In the situation

$$\tau_a = \tau_b \quad , \tag{3.3.77}$$

one can see

$$\hat{\gamma} = 1 \quad . \tag{3.3.78}$$

In the situation

$$\tau_a \gg \tau_b \tag{3.3.79}$$

when ζ_b isn't too small then

$$\hat{\gamma} \geq \frac{\sqrt{[\frac{\zeta_a}{\tau_a} - \frac{\zeta_b}{\tau_b}]^2 + 4\frac{(\zeta_a+1)(\zeta_b+1)}{\tau_a\tau_b}}\tau_b}{\zeta_b+1} \geq \frac{\zeta_b}{\zeta_b+1} \quad . \tag{3.3.80}$$

Choose the variables in the following manner

$$0 < \hat{\xi}_c < \hat{\xi}_+ \quad . \tag{3.3.81}$$

When $V \gg V_c$ then

$$\hat{\xi}_+ - \hat{\xi}_- \ll \hat{\xi}_+ - \hat{\xi}_c \quad . \tag{3.3.82}$$

Then one can put $\hat{\xi}$ to $\hat{\xi}_+$.

Consider the situation

$$\tau_a \gg \tau_b \quad , \quad \zeta_b \ll 1 \quad . \tag{3.3.83}$$

For the essential condensation it is necessary that $\zeta_a \geq 1$. Then $\hat{\xi} \ll 1$ and[29]

$$\frac{d\nu_a}{dt} = V^{2/3}\tau_a^{-1}(\zeta_a+1) \quad , \quad \frac{d\nu_b}{dt} = V^{2/3}\tau_b^{-1}(1 - \frac{\nu_b}{\nu_a+\nu_b}) \quad . \tag{3.3.84}$$

These relations can be rewritten as

$$\frac{d\nu_a}{dt} = \nu_b^{2/3}A \quad , \quad A = v_{l\,b}^{2/3}\frac{\zeta_a+1}{\tau_a} \quad , \quad \frac{d\nu_b}{dt} = \nu_b^{2/3}\frac{\nu_a}{\nu_b} \quad , \quad B = \frac{v_{l\,b}^{2/3}}{\tau_b} \quad . \tag{3.3.85}$$

[29]The situation $\zeta_a \gg 1$ is impossible. The inequality $\tau_a \gg \tau_b$ is very strong.

From the expression for $d\nu_a/dt$ one can get

$$\nu_a = A\int_{t_0}^{t} \nu_b^{2/3} dt \quad . \tag{3.3.86}$$

Then the expression for $d\nu_b/dt$ comes to

$$\frac{d\nu_b}{dt} = BAF(t)\nu_b^{-1/3} \quad , \tag{3.3.87}$$

where

$$F(t) = \int_{t_0}^{t} \nu_b^{2/3}(t')dt' \quad . \tag{3.3.88}$$

Consider F as the known value. Then this equation can be integrated as the differential equation of the first order. The initial condition for the function $y = \nu_b^{4/3}$ can be rewritten as

$$y = \frac{4}{3}BA\int_{t_1}^{t}\int_{t_0}^{t'} y(t'')dt''dt' \quad . \tag{3.3.89}$$

After the differentiation

$$\frac{d^2y}{dt^2} = \frac{4}{3}BAy^{1/2} \quad . \tag{3.3.90}$$

This equation doesn't contain t and can be integrated by the transition to $z = dy/dt$. This leads to

$$\frac{dz}{dy}z = \frac{4}{3}BAy^{1/2} \quad , \tag{3.3.91}$$

$$\ln z = \frac{8}{9}BAy^{3/2} + const_1 \quad . \tag{3.3.92}$$

The further integration gives

$$\frac{dy}{dt} = const_1 \exp(\frac{8}{9}BAy^{3/2}) \quad , \tag{3.3.93}$$

$$\frac{\int \exp(-\frac{8}{9}BAy^{3/2})dy}{const_1} = t + const_2 \quad . \tag{3.3.94}$$

The situation where the estimate from below to $\hat{\gamma}$ is absent can be described explicitly. æ

3.4 Multi component condensation in the dynamic conditions

Here the global evolution will be considered. The situation of the decay is also described by the corresponding remarks.

3.4.1 Flows and velocities

For the flows of the molecules on the droplets one can get

$$W_a^+(\{\nu_a\}) \sim v_{t\ a} S n_a \quad , \tag{3.4.1}$$

where v_{ta} are the thermal velocities, the coefficients of the condensation α_i can be included in the thermal velocity. These formulas can be rewritten as

$$W_a^+(\{\nu_a\}) = \frac{n_a}{n_{aa}} \frac{(\sum_b \nu_b v_{l\ b})^{2/3}}{\tau_a} \quad . \tag{3.4.2}$$

For W_a^+/W_b^+ one can get

$$\frac{W_a^+}{W_b^+} = \frac{v_{t\ a} n_a}{v_{t\ b} n_b} \quad , \tag{3.4.3}$$

which doesn't depend on the size of the droplet.

Determine the inverse flows. The equilibrium distribution has to satisfy

$$W_a^+ n^e(\{\nu_i\}) = W_a^-(\nu_a + 1, \{\nu_b\}_{b \neq a}) n^e(\nu_a + 1, \{\nu_b\}_{b \neq a}) \quad . \tag{3.4.4}$$

Due to

$$n^e(\{\nu_a\}) = \exp(-F(\{\nu_a\}))/\hat{N} \quad , \tag{3.4.5}$$

where $\hat{N}$ is the normalizing factor one can get for W_a^- the following expression

$$W_a^-(\nu_a + 1, \{\nu_b\}_{b \neq a}) = W_a^+ \exp(-F(\{\nu_a\}) + F(\nu_a + 1, \{\nu_b\}_{b \neq a})) \quad . \tag{3.4.6}$$

To justify the substitution of the finite differences by the derivatives one has to calculate the derivatives in the approximation of the independent concentrations

$$\frac{\partial F}{\partial \nu_a} = \frac{2a(\sum_b v_{l\ b} \nu_b)^{-1/3} v_{l\ a}}{3} - \ln(\frac{n_a}{n_{aa}}) + \ln(\xi_a) f_a(\xi_a) \rightarrow$$
$$- \ln(\frac{n_a}{n_{aa}}) + \ln(\xi_a) f_a(\xi_a) \quad , \tag{3.4.7}$$

$$\frac{\partial^2 F}{\partial \nu_a^2} \to\sim (\sum_b \nu_b)^{-1} \to 0 \quad . \tag{3.4.8}$$

To get these equations one has to take into account the Gibbs-Duhem equation

$$\sum_a \xi_a \frac{\partial b_a}{\partial \xi_i} + \frac{\hat{S}}{\sum_b \nu_b} \frac{\partial \gamma}{\partial \xi_i} = 0 \quad . \tag{3.4.9}$$

For the super critical embryo

$$\sum_a \xi_a \frac{\partial b_a}{\partial \xi_i} = 0 \quad . \tag{3.4.10}$$

This equation is used to exclude the cross terms $\partial F / \partial \nu_i$.

For the inverse flow

$$W_a^- = W_a^+ \frac{n_{aa} \xi_a}{n_a} f_a(\xi_a) \quad . \tag{3.4.11}$$

for the velocity of ν_a one can get

$$\frac{d\nu_a}{dt} = \frac{(\sum_b \nu_b v_{l\ b})^{2/3}}{\tau_a} (\frac{n_a}{n_{aa}} - \xi_a f_a(\xi_a)) \quad . \tag{3.4.12}$$

3.4.2 Supersaturation and ideal supersaturation

Introduce the supersaturations by

$$\zeta_a = \frac{n_a}{n_{aa}} \quad . \tag{3.4.13}$$

The laws of growth can be rewritten as

$$\frac{d\nu_i}{dt} = (\zeta_i - \xi_i f_i) \frac{(\sum_b \nu_b v_{l\ b})^{2/3}}{\tau_i} \quad . \tag{3.4.14}$$

Denote the ideal supersaturations via Φ_a. Then

$$\Phi_a = \frac{n_{tot\ a}}{n_{aa}} \quad . \tag{3.4.15}$$

Here $n_{tot\ a}$ is the total number of the molecules of the component a in the unit of volume.

Traditionally the smooth character of the ideal supersaturation is ensured by the power dependence on time. It is necessary to show that

if the power dependence is valid for one component it must be valid for the other components.

In the isochoric cooling

$$\Phi_a(T) = \Phi_a(T_o)\exp(-\beta_a\frac{T-T_o}{T_o}) \quad , \tag{3.4.16}$$

where β_a is the heat of the condensation of one molecule. When Φ_a satisfies to the power approximation

$$\Phi_a(t) = \Phi_a(t_o)(\frac{t-t_o}{t_\infty})^{m_a} \tag{3.4.17}$$

with parameters t_∞ and m_a then the temperature satisfies to

$$\frac{T-T_o}{T_o} = -\frac{m_a}{\beta_a}\ln(\frac{t-t_o}{t_\infty}) \quad . \tag{3.4.18}$$

Then for Φ_b one can get the expression

$$\Phi_b(t) = \Phi_b(t_o)(\frac{t-t_o}{t_\infty})^{(\beta_b m_a)/\beta_a} \quad . \tag{3.4.19}$$

This is also the power law with the parameters t_∞ and $m_b = m_a\beta_b/\beta_a$.

In the case of the isothermal compression

$$\Phi_a(t) = \Phi_a(t_o)\frac{V(t_o)}{V(t)} \quad , \tag{3.4.20}$$

where V is the volume and

$$\frac{\Phi_a(t)}{\Phi_b(t)} = \frac{\Phi_a(t_o)}{\Phi_b(t_o)} \quad . \tag{3.4.21}$$

Then the power approximation is valid for another component with the same parameters.

In the case of the adiabatic expansion the temperature and the volume of the system are connected by

$$T(t)V^{\gamma-1}(t) = T(t_o)V(t_o)^{\gamma-1} \quad , \tag{3.4.22}$$

where

$$\gamma = \frac{\sum_a n_{aa}\Phi_a c_{pa} + n_g c_{pg}}{\sum_a n_{aa}\Phi_a c_{va} + n_g c_{vg}} \quad , \tag{3.4.23}$$

where n_g is the molecule number density of the passive gas, $c_{pa}, c_{pg}, c_{va}, c_{vg}$ are the molecular heat capacities of the component a and the passive gas under the constant pressure and under the constant volume. Then

$$\Phi_a(T) = \Phi_a(T_0)(\frac{T}{T_o})^{\frac{1}{\gamma-1}} \exp(-\beta_b \frac{T-T_o}{T_o}) \quad , \tag{3.4.24}$$

$$\Phi_b(T) = \Phi_b(T_0)(\frac{T}{T_o})^{\frac{1}{\gamma-1}} \exp(-\beta_b \frac{T-T_o}{T_o}) \quad . \tag{3.4.25}$$

Due to $\beta_a \gg 1$ for the majority of the substances in the normal thermodynamic conditions the relative deviations of the temperature are small. We have the approximate result

$$(\frac{T}{T_o})^{\frac{1}{\gamma-1}} \approx \exp(\frac{T-T_o}{(\gamma-1)T_o}) \quad . \tag{3.4.26}$$

Then this case can be reduced to the case of the isochoric cooling with the renormalized parameters

$$\beta_a^+ = \beta_a - \frac{1}{\gamma-1} \quad , \qquad \beta_b^+ = \beta_b - \frac{1}{\gamma-1} \quad . \tag{3.4.27}$$

3.4.3 Stationary intensity of the embryos formation

One can analytically show that in the conditions of the applicability of the macroscopic description of the critical embryo it is possible to use the quasi stationary state of the near critical embryos and the main role in the vapor consumption is played by the super critical embryos.

Here we shall illustrate some approaches to the determination of the normalizing factor. It will be done on order to illustrate how doubtful is the meaning of the normalizing factor. According to the unequivalency of the ensembles these considerations can have the illustrative character.

For the stationary rate of nucleation one can have

$$J_s(\{\zeta_a\}) = Z(\sum_a n_a \Psi_a \exp(-\Delta_a F_c)) \quad , \tag{3.4.28}$$

where

$$\Psi_a = \frac{n_a}{\sum_b n_b} \quad , \tag{3.4.29}$$

$$\Delta_a F_c = F(\{\nu_{b\ c}\}) + \ln(n_a v_{l\ a}) \tag{3.4.30}$$

and the index c marks the critical embryo. The value of Z is the Zeldowitch factor [3] and it is the smooth function of the supersaturation. It

is extracted as all other terms except the equilibrium distribution in the expression for the stationary rate of nucleation. With the probability Ψ_a the critical embryo is formed on the molecule of the component a and to form the critical embryo it is necessary to pay the minimal work $\Delta_a F$. This work can be slightly changed due to the fluctuations.

These considerations are not more than the model. It can be corrected by the following way.

In the previous considerations the final volume of fixation depends on the sort of the molecule. It is more natural to define the final volume of fixation by the following way. Every thermodynamic value has the characteristic fluctuations. The center of mass of the critical embryo also has to fluctuate. The characteristic size of such fluctuation defines the final volume of fixation[30].

According to the thermodynamic expression for the free energy of the embryo formation the bottom of the channel of nucleation is the straight line. Then the most energetically profitable way for the embryo is the line $\xi_i = \xi_{i\ c}$. We come to the quasi onedimensional situation.

The addition of the molecule initiates the average transition of the center of mass to the distance

$$\frac{E\nu^{1/3}}{\nu+1} \approx E(\nu+1)^{-2/3}; \qquad E = const = (\frac{3(\sum_i \xi_{i\ c} v_{l\ i})}{4\pi})^{1/3} \quad ,$$

where ν is the total number of the molecules in the embryo. For the mean square of the fluctuation[31] of the position of the center of mass M one can get

$$((M-(M)_{av})^2)_{av} = (\sum_{l=2}^{\nu_c+1} El^{-2/3}k_l \sum_{m=2}^{\nu_c+1} Em^{-2/3}k_m)_{av} = \sum_{l=2}^{\nu_c+1} E^2 l^{-4/3} \quad ,$$

where $(...)_{av}$ is the averaging and k_l is the stochastic vector with ($|k_l| = 1$). Then the value of the volume V_{final}

$$V_{final} = \frac{4\pi}{3}(const \sum_{l=2}^{\nu_c+1} E^2 l^{-4/3})^3 \quad const \sim 1$$

and can be expressed through the ζ-function.

[30]It is more correct to define the distribution of the fluctuation of the size for every size. Then the exponent of the work of localization of the given volume has to averaged with this distribution.

[31]The total stochastic character of this process allows to construct also the distribution function. It will be the distribution of the Poisson type.

As far as the seria in the last equation converges one can put $\nu_c \to \infty$ in the thermodynamic limit. Note that in the condensation on the plane surface the power 4/3 can be substituted by 1 and the convergence of the last expression in the limit $\nu_c \to \infty$ doesn't take place. So, the comparison between the three dimension case and the plane case can lead to the extraction of the presence of such correction.

The stationary state of the embryos in the critical region leads to the following expression for the intensity of the droplets formation

$$J_s(\{\zeta_a\}) = Z^+ \exp(-F_c) \tag{3.4.31}$$

with the renormalizing factor

$$Z^+ = Z[\sum_j \frac{n_j}{\sum_i n_i} \frac{1}{v_{l\ j}}] \tag{3.4.32}$$

or

$$Z^+ = Z[\sum_j \frac{n_j}{\sum_i n_i} \frac{1}{V_{final}}] \quad .$$

The factor Z combines the rate of nucleation with the equilibrium distribution n^{eq} formally spread until the critical size. Then for the equilibrium distribution one can get

$$n^{eq} = [\sum_j \frac{n_j}{\sum_i n_i} \frac{1}{V_{final}}] \exp(-F) \quad . \tag{3.4.33}$$

The factor Z^+ is rather smooth function of the supersaturation in comparison with the exponential term in the expression for the stationary rate of nucleation.

* * *

The critical region is extracted by the condition

$$\mid F(\{\nu_i\}) - F_c \mid \leq const \sim 1 \quad . \tag{3.4.34}$$

The time of relaxation in the critical region can be estimated from above. The linear transformation can lead to the set $\nu_{*\ i}$ which reduces the square form of the free energy to the sum of the squares and $\nu_{*\ i}$ has the same scale as ν_i has. Because the set $\{\nu_{*\ 0} \sim \sum_j \nu_j v_{l\ j},\ \{\xi_i\}_{i=1}^{i=n-1}\}$ diagonolize the square form of the free energy it is simple to do. Then one can come to the following estimate from above

$$t_{rel} \approx \frac{(diam(\nu_c))^2}{W_c} \quad , \tag{3.4.35}$$

where

$$diam(\nu_c) \approx [\sum_j 2/(\mid \frac{\partial^2 F}{\partial \nu^2_{*\ j}} \mid)]^{1/2} \quad , \tag{3.4.36}$$

$$diam(\nu_c) \sim perim(\nu_c) \quad ,$$

$$perim\nu_c \approx \sum_j [2/(\mid \frac{\partial^2 F}{\partial \nu^2_{*\ j}} \mid)]^{1/2} \quad ,$$

$$W_c = min[W^+_{i\ c}] \tag{3.4.37}$$

and the derivatives are taken at the saddle point. This estimate can be established by the sequential consideration of the diffusion along the different variables. The long tails of the near critical region along the diagonals of the rectangular with the coordinates

$$\nu_{*\ i\ c} \pm (2/(\mid \frac{\partial^2 F}{\partial \nu^2_{*\ i}} \mid))^{1/2} \quad , \quad \nu_{*\ 0\ c} \pm (2/(\mid \frac{\partial^2 F}{\partial \nu^2_{*\ 0}} \mid))^{1/2}$$

can be excluded from the consideration[32]. Here $\nu_{*\ 0} \sim \sum_j \nu_j v_{l\ j}$ is the unstable variable with the same scale as the scale of $\nu_{*\ i}$ and the other variables are the stable variables.

3.4.4 Concentration of solution in droplets

The dynamic equations for ξ_i are the following

$$\frac{d\xi_i}{dt} = \frac{(\sum_b \nu_b v_{l\ b})^{2/3}}{\sum_j \nu_j} [\frac{\zeta_i - \xi_i f_i(\xi_i)}{\tau_i} - \xi_i \sum_j \frac{\zeta_j - \xi_j f_j(\xi_j)}{\tau_j}] \quad . \tag{3.4.38}$$

The first term isn't expressed through ξ_i, the set of the variables

$$\{\xi_i\}, \frac{(\sum_b \nu_b v_{l\ b})^{2/3}}{\sum_j \nu_j}$$

is used. The stationary solutions can be obtained from

$$\frac{\zeta_i - \xi_i f_i(\xi_i)}{\tau_i} = \xi_i \sum_j \frac{\zeta_j - \xi_j f_j(\xi_j)}{\tau_j} \quad . \tag{3.4.39}$$

[32]It is necessary to consider the essential part of the critical region without tails.

The values ξ_i aren't independent but satisfy the restriction

$$\sum_i \xi_i = 1 \quad . \tag{3.4.40}$$

On the base of the variables

$$\delta_i = \frac{\zeta_i - \xi_i f_i(\xi_i)}{\tau_i} \tag{3.4.41}$$

and

$$\Delta = \sum_j \delta_j \tag{3.4.42}$$

one can see that

$$\frac{\zeta_i - \xi_i f_i(\xi_i)}{\xi_i \tau_i} = \Delta \tag{3.4.43}$$

is invariant with respect to i. In the approximation of the ideal solution the equation (3.4.39) can be rewritten as

$$\delta_i = (\zeta_i - \delta_i \tau_i)\Delta \tag{3.4.44}$$

and gives the expression for δ_i through Δ. It leads to

$$1 = \sum_i \frac{\zeta_i}{1 + \tau_i \Delta} \quad . \tag{3.4.45}$$

The last equation satisfies to the normalizing condition (3.4.40).

Due to $\zeta > 0$, $\tau_i > 0$ the uniqueness of Δ is evident. The last equation is the algebraic equation of the power m of the number of the components.

One can see that this extremum is the stable one. On the base of Δ one can reconstruct concentrations with the help of (3.4.43). Only here the condition $\xi_i > 0$ will be used. The characteristic time can be found from

$$t_{relax} = max_i\{[\frac{d}{d\xi_i}(\frac{d\xi_i}{dt})]^{-1}\} \quad , \tag{3.4.46}$$

where the derivative is taken in the stationary point. All values have to be put to the magnitudes at PIFD. They can be found from the further consideration or from the simple estimates.

In the conditions of the macroscopic description of the critical embryo the following inequality

$$t_{relax} \ll \Delta_{PIFD} t \tag{3.4.47}$$

is valid. Here Δ_{PIFD} marks the characteristic variations of the magnitudes during PIFD. After the $\Delta_{PIFD}t$ is obtained this inequality can be justified directly.

3.4.5 Approximation of stationary intensity of nucleation

Denote some moment from PIFD as t_* and mark all values at this moment by the index $*$. For the height of the activation barrier one can get the following approximation

$$F_c(\{\zeta_a\}) = F_c(\{\Phi_{a\ *}\}) + \sum_i \frac{dF_c}{d\zeta_i} \mid_{\zeta_i = \Phi_{i\ *}} (\zeta_i - \Phi_{i\ *}) \quad . \tag{3.4.48}$$

One can get some estimates for the derivatives in this approximation

$$\frac{dF_c}{db_a} = \frac{\partial F}{\partial b_a} \mid_c + \sum_b \frac{\partial F}{\partial \nu_b} \mid_c \frac{\partial \nu_{b\ c}}{\partial b_a} + \sum_{b \neq a} \frac{\partial F}{\partial b_b} \mid_c \frac{\partial b_b}{\partial b_a} \quad . \tag{3.4.49}$$

One has to see that in the range of the supersaturations corresponding to the inverse value of the derivative the variation of the derivative is negligible. Then one can see that the last term of the previous relation is important due to

$$b_i = 2av_{l\ i} \quad \frac{\nu_+^{-1/3}}{3} \tag{3.4.50}$$

in the saddle point. Here

$$\nu_+ = \sum_b v_{l\ b} \nu_b \tag{3.4.51}$$

and

$$b_a = b_b \frac{v_{l\ a}}{v_{l\ b}} \tag{3.4.52}$$

in the saddle point. Then

$$\frac{dF_c}{db_i} = -\frac{\nu_{+\ c}}{v_{l\ i}} \quad . \tag{3.4.53}$$

We can see this formula also by the differentiation of the explicit result

$$F_c = \frac{a\nu_{+\ c}^{2/3}}{3} \quad . \tag{3.4.54}$$

Introduce

$$\Gamma_i = -\zeta_i \frac{dF_c}{d\zeta_i} \sim \frac{\nu_{+\ c}}{v_{l\ i}} \quad . \tag{3.4.55}$$

Under the macroscopic description these values are the big ones in comparison with 1. Then the relative variation of ζ_a during PIFD has the order less or equal than Γ_a^{-1}. During PIFD

$$\mid \frac{\zeta_i - \Phi_{i\ *}}{\Phi_{i\ *}} \mid \leq \Gamma_{i\ *}^{-1} \quad . \tag{3.4.56}$$

It is also possible to prove that during PIFD there is no compensation of the increase of one component by the decrease of the other component.

Then one can come to the following approximation

$$J_s(\{\zeta_a\}) = J_s(\{\Phi_{a\ *}\}) \exp(\sum_i \Gamma_{i\ *} \frac{\zeta_i - \Phi_{i\ *}}{\Phi_{i\ *}}) \quad . \tag{3.4.57}$$

3.4.6 Period of intensive formation of droplets

During PIFD one can keep

$$\zeta_a = \Phi_{a\ *} \quad . \tag{3.4.58}$$

Consider ξ_a as $\xi_a(\{\Phi_{b\ *}\})$. One can get for the droplets

$$\nu_a = \frac{\xi_a}{\xi_b} \nu_b \quad , \tag{3.4.59}$$

$$\frac{d\nu_a}{dt} = \frac{\xi_a}{\xi_b} \frac{d\nu_b}{dt} \quad . \tag{3.4.60}$$

For the rate of nucleation one can have

$$\frac{d\nu_a}{dt} = \nu_a^{2/3} [(\sum_b \frac{\xi_b}{\xi_a} v_{l\ b})^{2/3} (\zeta_a - \xi_a f_a)] / \tau_a \quad . \tag{3.4.61}$$

For the variables

$$\rho_a = \nu_a^{1/3} \tag{3.4.62}$$

the rate of growth doesn't depend on the values of these variables

$$\frac{d\rho_a}{dt} = (\sum_b \xi_b v_{l\ b})^{2/3} \xi_a^{-2/3} (\zeta_a - \xi_a f_a) / (3\tau_a) = \lambda_a \quad . \tag{3.4.63}$$

Introduce z_a as the coordinates ρ_a of the droplet formed at $t = t_*$. Then

$$z_a = \int_{t_*}^{t} \frac{d\rho_a}{dt} dt = \lambda_a (t - t_*) \quad . \tag{3.4.64}$$

Instead of the distribution on $\{\nu_a\}, t$ one can use the distribution on $\{\rho_a\}, t$. Denote it by f and keep this definition here and in the next section. Together with $f(\{\rho_a\}, t)$ consider also the squeezed distributions $f_a(\rho_a, t)$. The integral over the distribution gives the total number of the droplets in the unit of volume. Kinetic equation can be rewritten as

$$\frac{\partial f_i}{\partial t} = -\frac{\partial f_i}{\partial \rho_i} \frac{d\rho_i}{dt} \tag{3.4.65}$$

with the known solution

$$f_i(\rho_i, t) = f_i(x_i) \quad , \qquad x_i = z_i - \rho_i \quad . \tag{3.4.66}$$

To get the form of the function $f_a(x_a)$ one can use the boundary condition at the small sizes. One can put this condition between the near critical region and the post critical region. One can analytically justify the quasi stationary approximation under the conditions of the macroscopic description of the critical embryo. Then

$$f_i(\rho_i, t) \mid_{\rho_i = 0} = J_s (\frac{d\rho_i}{dt})^{-1} = \frac{J_s}{\lambda_i} = f_{s\ i} \quad . \tag{3.4.67}$$

Then the solution of the kinetic equation has the form

$$f_i(x_i) = f_{s\ i}(\{\zeta_a(x_i)\}) \quad . \tag{3.4.68}$$

Due to

$$\xi_b^{1/3} x_a = \xi_a^{1/3} x_b \quad , \qquad \xi_a^{1/3} f_a(x_a) = \xi_b^{1/3} f_b(x_b) \tag{3.4.69}$$

one can consider only one solution.

3.4.7 Balance equation

To get the dependence of ζ_a, f_a on time and on x_i it is necessary to consider the equation of the balance of the substance. Denote the number of the molecules of the component a condensated in all droplets by $n_{aa} g_a$. Then for g_a one can get

$$g_a = \int_{-\infty}^{z_a} (z_a - x_a)^3 \frac{f_a(x_a)}{n_{aa}} dx_a \quad . \tag{3.4.70}$$

Between g_a and g_b there is the simple connection

$$g_b = g_a \frac{n_{aa}\xi_b}{\xi_a n_{bb}} \quad . \tag{3.4.71}$$

The balance equations can be written as

$$\Phi_i = \zeta_i + g_i \quad . \tag{3.4.72}$$

Linearize the ideal supersaturation as the function of x_a

$$\Phi_a = \Phi_{a\,*} + k_a x_a \quad . \tag{3.4.73}$$

After the final results one can check the validity of this approximation.

On the base of the of the approximation for the rate of nucleation one can get for the stationary distribution

$$f_{s\,a}(\{\zeta_a\}) = f_{s\,a}(\{\Phi_{a\,*}\}) \exp(\sum_i \Gamma_{i\,*} \frac{\zeta_i - \Phi_{i\,*}}{\Phi_{i\,*}}) \quad . \tag{3.4.74}$$

Taking into account the balance equation and the linearization one can get

$$f_{s\,a}(\{\zeta_a(x_a)\}) = f_{s\,a}(\{\Phi_{a\,*}\}) \exp(kx_a - qg_a(x_a)) \quad , \tag{3.4.75}$$

where

$$k = \sum_b \frac{\Gamma_{b\,*} k_b \xi_b^{1/3}}{\Phi_{b\,*} \xi_a^{1/3}} \quad , \tag{3.4.76}$$

$$q = \sum_b \frac{\Gamma_{b\,*} n_{aa} \xi_b}{\xi_a n_{bb} \Phi_{b\,*}} \quad . \tag{3.4.77}$$

Then one can get the closed equation for $g_a(z_a)$

$$g_a(z_a) = \frac{J_s(\{\Phi_{a\,*}\})}{\lambda_a n_{aa}} \int_{-\infty}^{z_a} (z_a - x_a)^3 \exp(kx_a - qg_a) dx_a \quad . \tag{3.4.78}$$

The structure of this equation coincides with the one component case. This equation can be solved by the methods of the second chapter.

The algebraic equation on the parameters of the condensation can be written in the following form

$$J_s(\{\Phi_a\}) q = k^4 n_{aa} \lambda_a const \quad . \tag{3.4.79}$$

The value of *const* depends on the concrete choice of t_*. When t_* is chosen as the moment of the maximum of the supersaturation or as the moment when the half of the total numbers of the droplets is formed then the calculation can be fulfilled according to the second chapter. The algebraic equation for the parameters can be solved by iterations where

$$\exp(-F_c(\{\Phi_{a\ *}\}))$$

is unknown part. In the reconstruction of t_* and $\Phi_{a\ *}$ on the base of F_c one can construct the internal iterations.

3.4.8 Decay of the multi component system

The important place in the external conditions is occupied by the decay of the metastable system. This case can be investigated formally when $k = 0$ and $\Phi_{j\ *}$ is considered as the known parameter. One has to integrate in the balance equation from the moment t_*. Then the balance equation has the following form

$$Q_a(z_a) = \frac{J_s(\{\Phi_{a\ *}\})q}{\lambda_a n_{aa}} \int_0^{z_a} (z_a - x_a)^3 \exp(-Q_a) dx_a \qquad (3.4.80)$$

for the value

$$Q_a = qg_a$$

After the transition to the variables

$$z_a \to z_a (\frac{J_s(\{\Phi_{a\ *}\})q}{\lambda_a n_{aa}})^{1/4}$$

$$x_a \to x_a (\frac{J_s(\{\Phi_{a\ *}\})q}{\lambda_a n_{aa}})^{1/4}$$

one can get the equation

$$Q_a(z_a) = \int_0^{z_a} (z_a - x_a)^3 \exp(-Q_a) dx_a \quad , \qquad (3.4.81)$$

which doesn't contain parameters.

It has the universal solution and allows the same conclusions which have been made in the situation of the dynamic conditions.

* * *

The equivalency of the multi component case and the one component case plays a very important role. The formal correspondence in ensured

by the similar regimes of the vapor consumption. But the regime of the consumption of one component can differ from the regime of the consumption of the other component. Then this equivalency can not be attained now. The precise equivalency have to be substituted by the approximate equivalency on the level of the first iterations. It will be easily seen later after the conception of the universal solution will be formulated in the chapter six.

* * *

Heterogeneous condensation

As far as the form of equations of the kinetics of the condensation is absolutely analogous to the one component case the effects of the heterogeneous nucleation can be introduced analogously to the second chapter.

3.4.9 The further evolution in the dynamic conditions

We shall use the approximation of the ideal solution. The generalizations are obvious.

Analogously to the situation of the simultaneous creation of the ideal supersaturation the spectrum can be considered as the monodisperse one after the final of PIFD. Then the equations of the condensation can be written as

$$\frac{d\nu_i}{dt} = \frac{S}{\tau_i}(\zeta_i - \frac{\nu_i}{\sum_b \nu_b} f_i(\frac{\nu_i}{\sum_b \nu_b})) \quad , \tag{3.4.82}$$

where $S = (\sum_b v_{l\ b}\nu_b)^{2/3}$. For the arbitrary component of the embryo with the given S the increase of ν_a initiates the decrease of $\frac{d\nu_a}{dt}$ and the increase of $\frac{d\nu_b}{dt}$ for the other component. Analogously, the increase of ν_b leads to the decrease of $\frac{d\nu_b}{dt}$ and to the increase of $\frac{d\nu_a}{dt}$. So, the spectrum is the monodisperse on ξ_i. From the last equation it follows that

$$\frac{dS^{1/2}}{dt} = \sum_a \frac{\zeta_a - \xi_a f_a(\xi_a)}{3\tau_a} v_{l\ a} \tag{3.4.83}$$

and the velocity of the growth of $S^{1/2}$ depends only on ξ_a. Then it is constant for all embryos. As far as at the end of PIFD the spectrum of almost monodisperse on the extensive variable it will be monodisperse until the coalescence.

In the monodisperse on $S^{1/2}$ and on ξ_a approximation the system of the condensation equations can be written in the following form

$$\frac{d\nu_i}{dt} = \frac{1}{\tau_i}(\sum_b \nu_b v_{l\ b})^{2/3}(\Phi_i - N\frac{\nu_i}{n_{ii}} - \xi_i f_i(\xi_i)) \quad , \tag{3.4.84}$$

where N is the total number of the droplets.

Analyze the situation on the example of the isothermal evolution with the source of the vapor which is homogeneous in space. It allow to chancel some negligible parameters. If $m_a \leq 3$, then PIFD can not be reproduced more times as the number of the components. To construct the further PIFD one has to apply the methods from the second and from the forth chapter devoted to the embryos formation under the essentially non linear behavior of the external conditions.

Here we shall consider the solutions with the given N.

One can use some methods from [79]. All coefficients of activity must be introduced where the concentration appears. One can get the following equation on S

$$\frac{dS^{1/2}}{dt} = \sum_a [\Phi_a - \frac{N\nu_a}{n_{aa}} - \frac{\nu_a}{\sum_b \nu_b}]v_{l\ a}/(3\tau_a) \quad . \tag{3.4.85}$$

In the initial approximation one can suppose that S satisfies the equation

$$\frac{dS^{1/2}}{dt} = \sum_a [\Phi_a - \xi_a(\{\Phi_a\})]v_{l\ a}/(3\tau_a) \quad , \tag{3.4.86}$$

which can be integrated. After S as the function of time is obtained one can get ν_a as the functions of time from the differential equations of the first order

$$\frac{d\nu_a}{dt} = \frac{S}{\tau_a}(\Phi_a - N\frac{\nu_a}{n_{aa}} - \xi_a(\{\Phi_a\})) \quad . \tag{3.4.87}$$

So, we have fulfilled the first step of the iteration procedure which can be directly fulfilled. The values $S(t), \nu_a(t), \nu_b(t)$ are the initial values in the iteration procedure

$$\frac{dS^{1/2}_{(i+1)}}{dt} = \sum_a \frac{v_{l\ a}}{3\tau_a}(\Phi_a - \frac{N\nu_{a\ (i)}}{n_{aa}} - \frac{\nu_{a\ (i)}}{\sum_b \nu_{b\ (i)}}) \quad , \tag{3.4.88}$$

$$\frac{d\nu_{a\ (i+1)}}{dt} = \frac{S_{(i+1)}}{\tau_a}(\Phi_a - N\frac{\nu_{a\ (i+1)}}{n_{aa}} - \frac{\nu_{a\ (i)}}{\sum_b \nu_{b\ (i)}}) \quad . \tag{3.4.89}$$

Under the investigation of the final period one can take for the initial approximation the values ν_a corresponding to the situation when the whole substance except the saturated vapor is in the droplets. Then

$$\Phi_a = N\frac{\nu_{a\ lim}}{n_{aa}} + \frac{\nu_{a\ lim}}{\sum_b \nu_{b\ lim}} \quad . \tag{3.4.90}$$

Then one can get S in the initial approximation as

$$S_{lim} = (\sum_b \nu_{b\ lim} v_{l\ b})^{2/3} \quad . \tag{3.4.91}$$

When the supersaturations are greater than unity one can neglect $\nu_a / \sum_b \nu_b$. To have the intensive droplets formation it is necessary

$$\Phi_a \gg 1 \tag{3.4.92}$$

for some component "a".

Another opportunity is to substitute

$$\frac{\nu_a}{\sum_b \nu_b} \to \frac{\nu_{a\ lim}}{\nu_{a\ lim} + \sum_{b \neq a} \nu_b} \quad . \tag{3.4.93}$$

Also one can investigate the final period on the base of approximation

$$\nu_b = \nu_{b\ lim} \quad . \tag{3.4.94}$$

This approximation is connected with the iteration procedure

$$\frac{d\nu_{a\ (i)}}{dt} = \frac{S_{(i)}}{\tau_a}(\Phi_a - N\frac{\nu_{a\ (i+1)}}{n_{aa}} - \frac{\nu_{a\ (i)}}{\sum_b \nu_{b\ (i)}}) \quad , \tag{3.4.95}$$

$$S_{(i)} = (\sum_a v_{l\ a} \nu_{a\ (i)})^{2/3} \quad . \tag{3.4.96}$$

The composition of the different approximations for the different components is also effective in the description of the intermediate situations. Also one has to take into account the stochastic diffusion of the spectrum.

3.4.10 The further evolution in the situation of decay

Transform to the variables ξ_i and γ

$$\gamma = (\sum_b \nu_b v_{l\ b})^{1/3} \quad . \tag{3.4.97}$$

It is obvious that

$$\frac{d\nu_a}{dt} = \frac{\gamma^2}{\tau_a}(\zeta_a + 1 - \xi_a) \quad . \tag{3.4.98}$$

Considering γ as parameter one can see that the spectrum becomes more and more monodisperse. The equation for γ

$$\frac{d\gamma}{dt} = \frac{1}{3}\sum_a v_{l\ a}\frac{\zeta_a + 1 - \xi_a}{\tau_a} \equiv \lambda \tag{3.4.99}$$

shows that when the spectrum is monodisperse on ξ_i the evolution on γ has the stable character. Then the spectrum is monodisperse also in ξ_i, γ (or in ν_i).

The condensation equations have the following form

$$\frac{d\nu_a}{dt} = \frac{(\sum_b v_{l\ b}\nu_b)^{2/3}}{\tau_a}(\Phi_a + 1 - \xi_a - N\frac{\nu_a}{n_{aa}}) \quad . \tag{3.4.100}$$

The initial conditions are rather evident

$$\nu_a(t=0) = 0 \quad . \tag{3.4.101}$$

The values ν_a represents the coordinates of the monodisperse peak. The ratio ν_a/ν_b depends on time.

Consider the situation $\zeta_a \gg 1$ for all ζ_a. Then for all ξ_i, with one and the same scale

$$\frac{d\nu_i}{dt} = \frac{\gamma^2}{\tau_i}(\Phi_i - N\frac{\nu_i}{n_{ii}}) \quad . \tag{3.4.102}$$

This system of equations can not be solved analytically. The next simplification is to consider γ as the known function of time. The values ν_a in the expression for γ are considered as been formed under the ideal supersaturation. Then

$$\gamma = \lambda(\{\Phi_a\})t$$

and this equation can be integrated

$$\Phi_i - N\frac{\nu_i}{n_{ii}} = \Phi_i \exp(-N\frac{\lambda^2 t^3}{3n_{ii}\tau_i}) \quad . \tag{3.4.103}$$

The errors can be estimated by the comparison with the one dimensional case. The error in ρ is less than 0,047. In the one dimensional case this approximation allows to inverse the dependence of t on ρ.

When the supersaturations are small in comparison with their initial values the methods from [79] can be used.

The deviation of v from 1 (not the deviation of n_{aa}/n_{bb} from 1) leads to the exhaustion of one component. One can see that for $\zeta_a, \zeta_b \gg 1$

$$\frac{dg_a}{dt} \approx \frac{n_{bb}\tau_b\zeta_a}{n_{aa}\tau_a\zeta_b}\frac{dg_b}{dt} \approx \frac{\zeta_a v_{t\ a}}{\zeta_b v_{t\ b}}\frac{dg_b}{dt} \approx \frac{\zeta_a}{\zeta_b}\frac{dg_b}{dt} \quad . \tag{3.4.104}$$

The last equation is valid when the thermal velocities of the molecules of different components have one and the same order. So, all components are exhausted and there is no further formation of the droplets.

Chapter 4

Nucleation on the different types of heterogeneous centers

The results of the previous chapter leads to the conclusion that the description of the more complicate situations can be given with help of anzats formulated on the base of the already known situations. But the direct application can lead to some errors. Even the case of the simultaneous heterogeneous and homogeneous decay of the metastable phase has some specific features in the construction of the analytical description.

4.1 Theory of homogeneous and heterogeneous decay of metastable phase

This theory will be valid also for the pure homogeneous condensation. At first we shall construct the description of PIFD.

4.1.1 The system of the condensation equations

Suppose that N is the number of the heterogeneously formed droplets and N^{∞} is the number of the homogeneously formed droplets. The upper index ∞ will mark the values for the homogeneous formation of

the droplets. The argument ∞ marks the total values of the magnitudes attained during the whole process of the condensation.

Immediately after the creation of the initial supersaturation the value of the supersaturation goes to

$$\Phi_* = \zeta(0) - \frac{\eta_{tot}\nu_e}{n_\infty} \quad , \tag{4.1.1}$$

where ν_e is the number of the molecules in the equilibrium embryo. One can consider ν_e as the constant value during PIFD and take it at $\zeta = \Phi_*$. Ordinary ν_e can be taken at $\zeta = \zeta(0)$.

The following statements can be analytically justified:

(1) The main role in the vapor consumption is played by the super critical embryos, i.e. by the droplets.

(2) During the PIFD the quasi stationary approximation for the rate of nucleation is valid.

The justification of the second statement requires the expression for the time t^s of the establishing of the stationary state in the near critical region. For the majority of the types of heterogeneous centers and for the homogeneous process the rates of nucleation J and J^∞ during PIFD can be approximated as

$$J = J(\eta_{tot}, \Phi_*) \exp(\Gamma \frac{(\zeta - \Phi_*)}{\Phi_*}) \frac{\eta}{\eta_{tot}} \quad , \tag{4.1.2}$$

$$J^\infty = J^\infty(\Phi_*) \exp(\Gamma^\infty \frac{(\zeta - \Phi_*)}{\Phi_*}) \quad , \tag{4.1.3}$$

where

$$\Gamma = -\Phi_* \frac{d\Delta F(\zeta)}{d\zeta} \mid_{\zeta=\Phi_*} \quad , \tag{4.1.4}$$

$$\Gamma^\infty = -\Phi_* \frac{dF_c(\zeta)}{d\zeta} \mid_{\zeta=\Phi_*} \tag{4.1.5}$$

and ΔF is the height of the activation barrier, F_c is the free energy of the critical embryo formed homogeneously. The validity of these approximations can be justified for the homogeneous process and for the heterogeneous process with the interaction weaker than the reciprocal to the space distance.

Let f_* be the amplitude of the spectrum in the units of n_∞. As far as the initial supersaturation Φ_* and the total number of heterogeneous centers η_{tot} are some given values this value can be easily calculated by

the formulas of the first chapter. Let f_*^∞ be the analogous value for the homogeneous process.

The value $n_\infty g$ will mark the total number of the molecules in the droplets. The analogous value for the homogeneous process will be marked by g^∞. We shall also use $\theta = \frac{\eta}{\eta_{tot}}$.

One can get for g, g^∞, θ the following equations

$$g = f_* \int_0^z (z-x)^3 \exp(-\Gamma \frac{g+g^\infty}{\Phi_*})\theta dx \equiv G(g+g^\infty, \theta) \quad , \tag{4.1.6}$$

$$g^\infty = f_*^\infty \int_0^z (z-x)^3 \exp(-\Gamma^\infty \frac{g+g^\infty}{\Phi_*})dx \equiv G^\infty(g+g^\infty) \quad , \tag{4.1.7}$$

$$\theta = \exp(-f_* \frac{n_\infty}{\eta_{tot}} \int_0^z \exp(\Gamma \frac{g+g^\infty}{\Phi_*})dx) \equiv S(g+g^\infty) \quad . \tag{4.1.8}$$

These equations form the system of the condensation equations. As far as we determine the accuracy in the terms of the error in the total number of the droplets these values will be defined as

$$N = \eta_{tot}(1-\theta(z)) \equiv Q(\theta) \quad , \tag{4.1.9}$$

$$N^\infty = n_\infty f_*^\infty \int_0^z \exp(-\Gamma^\infty \frac{g+g^\infty}{\Phi_*})dx \equiv R(g+g^\infty) \quad . \tag{4.1.10}$$

4.1.2 Analysis of the standard iteration procedure

The formal generalization of the one dimension case (which has been done in [62]) leads to

$$g_{i+1} = G(g_i + g_i^\infty, \theta_i) \quad , \tag{4.1.11}$$

$$g_{i+1}^\infty = G^\infty(g_i + g_i^\infty) \quad , \tag{4.1.12}$$

$$\theta_{i+1} = S(g_i + g_i^\infty) \quad , \tag{4.1.13}$$

$$g_0 = 0 \quad , \tag{4.1.14}$$

$$N_i = Q(\theta_i) \quad , \tag{4.1.15}$$

$$N_{i+1}^\infty = R(g_i + g_i^\infty) \quad , \tag{4.1.16}$$

$$g_0^\infty = 0 \quad , \tag{4.1.17}$$

$$\theta_0 = 1 \quad , \tag{4.1.18}$$

$$g_1 = f_* \frac{z^4}{4} \quad , \tag{4.1.19}$$

$$g_1^\infty = f_*^\infty \frac{z^4}{4} \quad , \tag{4.1.20}$$

$$\theta_1 = \exp(-f_* \frac{n_\infty}{\eta_{tot}} z) \quad , \tag{4.1.21}$$

$$N_2^\infty(\infty) = f_*^\infty (\frac{\Gamma^\infty}{4\Phi_*})^{-1/4} (f_* + f_*^\infty)^{-1/4} A n_\infty \quad , \tag{4.1.22}$$

$$A = \int_0^\infty \exp(-x^4) dx \approx 0.9 \quad , \tag{4.1.23}$$

$$N_2(\infty) = \eta_{tot}[1 - \exp(-f_* \frac{n_\infty}{\eta_{tot}} (\frac{\Gamma}{4\Phi_*})^{-1/4} (f_* + f_*^\infty)^{-1/4} A)] \quad . \tag{4.1.24}$$

Analyze the expression for N_2^∞. Suppose that $f_* \gg f_*^\infty$. Decrease η_{tot} keeping f_* constant by the formal increase of the activity of the heterogeneous centers. When η_{tot} is small then the total number of the droplets coincides with the total number of the heterogeneous centers which goes to zero. The value g can be estimated from above as

$$g \leq \eta_{tot} z^3 \quad ,$$

The value of z at the end of PIFD must be put to Δx which is the width of the spectrum of the homogeneously formed droplets. The value Δx is restricted from above by $\Delta_\infty x$ which is the width of the spectrum of the droplets formed homogeneously without any influence of the heterogeneously formed droplets. The value $\Delta_\infty x$ doesn't depend on η_{tot} and f_*. So, the influence of the heterogeneously formed droplets on the process of the homogeneous condensation is negligible in the limit $\eta_{tot} \to 0$. The expression (4.1.22) for N^∞ shows that in the limit $\eta_{tot} \to 0$, $f_* = const$ the influence of the heterogeneously formed droplets is unessential. It leads to the giant error in N^∞ and in the total number of the droplets $N + N^\infty$. The problem is that one can not get the analytical expressions for N and N^∞ in frames of the third iteration.

For further considerations it is possible to adopt

$$f_*^\infty \ll f_* \quad . \tag{4.1.25}$$

Estimate N as

$$N \sim f_* \Delta_{\zeta\eta} x \quad ,$$

where $\Delta_{\zeta\eta}$ is the width of the spectrum of the heterogeneously formed droplets. The value of N^∞ can be estimated as

$$N^\infty \sim f^\infty \Delta x \quad .$$

On the base of these estimates one can come to the following statement: In all situations except those when $N^\infty \ll N$ the following inequality is valid

$$\Delta_{\zeta\eta} x \ll \Delta x \quad . \tag{4.1.26}$$

The relations presented above allow to justify analytically two approximations. The first one states that the process of the heterogeneous formation of the droplets can be described without any account of the homogeneous condensation.

4.1.3 Heterogeneous condensation

For the process of the heterogeneous formation of the droplets the following equations are valid

$$g = f_* \int_0^z (z-x)^3 \exp(-\Gamma \frac{g(x)}{\Phi_*}) \theta dx \equiv G(g,\theta) \quad , \tag{4.1.27}$$

$$\theta = \exp(-f_* \frac{n_\infty}{\eta_{tot}} \int_0^z \exp(-\Gamma \frac{g(x)}{\Phi_*}) dx) \equiv S(g) \quad . \tag{4.1.28}$$

Two last equations form the closed system. It can be solved by iterations

$$g_{i+1} = G(g_i, \theta_i) \quad , \tag{4.1.29}$$

$$\theta_{i+1} = S(g_i) \quad , \tag{4.1.30}$$

$$N_i = Q(\theta_i) \quad . \tag{4.1.31}$$

The operators G, S and Q have some properties. If for values of the arguments

$$w_1 \leq w_2 \quad ,$$

then

$$S(w_1) \leq S(w_2)$$

for all values of the arguments. If for all values of the arguments

$$w_1 \leq w_2 \quad ,$$

then

$$Q(w_1) \geq Q(w_2)$$

for all values of the arguments. If for values of the arguments

$$w_1 \leq w_2 \quad ,$$

$$v_1 \geq v_2 \quad ,$$

then

$$G(v_1, w_1) \leq G(v_2, w_2)$$

for all values of the arguments. The initial approximations will be chosen as

$$g_0 = 0 \quad , \tag{4.1.32}$$

$$\theta_0 = 1 \quad . \tag{4.1.33}$$

As far as

$$g_0 \leq g \quad ,$$

$$g_0 \leq g_i$$

for arbitrary i and

$$\theta_0 \geq \theta \quad ,$$

$$\theta_0 \geq \theta_i$$

for arbitrary i then the following estimate

$$N_2 \leq N \leq N_3 \tag{4.1.34}$$

is valid. The calculation gives

$$g_1 = f_* \frac{z^4}{4} \quad , \tag{4.1.35}$$

$$\theta_1 = \exp(-f_* \frac{n_\infty}{\eta_{tot}} z) \quad , \tag{4.1.36}$$

$$N_2(\infty) = \eta_{tot}(1 - \exp(-f_* \frac{n_\infty}{\eta_{tot}} (\frac{\Gamma}{4\Phi_*})^{-1/4} f_*^{-1/4} A)) \quad . \tag{4.1.37}$$

One can show that

$$\frac{d}{dx} \mid N_i - N_j \mid \geq 0 \quad , \tag{4.1.38}$$

and having calculated $N_3(\infty)$ one can get

$$\frac{\mid N_2 - N \mid}{N} \leq 0.015 \quad .$$

In the situation $N(\infty) \sim N^\infty(\infty)$ one can have $N(\infty) = \eta_{tot}$, i.e. all heterogeneous centers are exhausted. When $N(\infty) \neq \eta_{tot}$ then $\Delta_{\zeta\eta} x \sim \Delta x$ and $N(\infty) \gg N^\infty(\infty)$.

4.1.4 Spectrum of the homogeneously formed droplets

The further approximation is based on some expression for g. On the base of

$$\eta_{tot}(\Delta x)^3 \leq \frac{\Phi_*}{\Gamma^\infty} \tag{4.1.39}$$

and (4.1.26) one can note that the monodisperse approximation for g has some error only when

$$g(z) \ll \frac{\Phi_*}{\Gamma^\infty} \quad . \tag{4.1.40}$$

But the last inequality means that the influence of the heterogeneously formed droplets on the homogeneous process is negligible.

Monodisperse approximation for g leads to the following equation for g^∞

$$g^\infty = f_*^\infty \int_0^z (z-x)^3 \exp(-\Gamma^\infty \frac{g^\infty + \frac{N(\infty)}{n_\infty} x^3}{\Phi_*}) dx \quad , \tag{4.1.41}$$

where N is considered as the known value. The equation on

$$\lambda = g^\infty + \frac{N(\infty)}{n_\infty} z^3$$

can be written in the following from

$$\lambda(z) = f_*^\infty \int_0^z (z-x)^3 \exp(-\Gamma^\infty \frac{\lambda}{\Phi_*}) dx + \frac{N(\infty)}{n_\infty} z^3 \quad . \tag{4.1.42}$$

This equation can be solved by iterations

$$\lambda_{i+1} = G^\infty(\lambda_i) + \frac{N(\infty)}{n_\infty} z^3 \quad , \tag{4.1.43}$$

$$N_{i+1}^\infty = R(\lambda_i) \quad . \tag{4.1.44}$$

The operators G^∞ and R have the properties analogous to the properties of G,Q and S. If

$$w_1 \leq w_2$$

for all values of the arguments then

$$G^\infty(w_1) \geq G^\infty(w_2)$$

for all values of the arguments. If for all values of the arguments

$$w_1 \leq w_2 \quad ,$$

then

$$R(w_1) \geq R(w_2)$$

for all values of the arguments. Then having started from

$$\lambda_0 = 0 \tag{4.1.45}$$

and taking into account that

$$\lambda_0 \leq \lambda$$

and

$$\lambda_0 \leq \lambda_i$$

for arbitrary i with the help of the properties of the operators R and G^{∞} one can get

$$N_2^{\infty} \leq N^{\infty} \leq N_3^{\infty} \quad . \tag{4.1.46}$$

The calculation gives

$$\lambda_1 = f_*^{\infty} \frac{z^4}{4} + \frac{N(\infty)}{n_{\infty}} z^3 \quad , \tag{4.1.47}$$

$$N_2^{\infty} = f_*^{\infty} \int_0^z \exp(-(\frac{x}{\Delta_{\infty} x})^4 - (\frac{x}{\Delta_h x})^3) dx n_{\infty} \quad , \tag{4.1.48}$$

where

$$\Delta_{\infty} x = (\frac{4\Phi_*}{\Gamma^{\infty} f_*^{\infty}})^{1/4}$$

and

$$\Delta_h x = (\frac{\Phi_* n_{\infty}}{\Gamma^{\infty} N(\infty)})^{1/3} \quad .$$

The value $\Delta_{\infty} x$ can be imagined as the width of the spectrum when the heterogeneous process has the negligible influence. The value $\Delta_h x$ can be imagined as the width of the spectrum when the consumption of the vapor has the negligible influence.

One can show that

$$\frac{d}{dx} \mid N_i^{\infty} - N_j^{\infty} \mid \geq 0$$

and

$$\frac{d}{dN(\infty)} \mid N_i^\infty - N_j^\infty \mid \leq 0$$

for $i, j \geq 2$. Then

$$\frac{\mid N_2^\infty - N^\infty \mid}{N^\infty} \leq 0.015$$

by means of the calculation of $N_2^\infty(\infty)$ and $N_3^\infty(\infty)$ at $N(\infty) = 0$.

To get the qualitative analytical approximation one can note that

$$N_2^\infty(\infty) \approx f_*^\infty \Delta_\infty x (\frac{A}{2}(1 + (\frac{\Delta_\infty x}{\Delta_h x})^4)^{-1/4} + \frac{B}{2}(1 + (\frac{\Delta_\infty x}{\Delta_h x})^3)^{-1/3}) n_\infty \quad , \tag{4.1.49}$$

where

$$B = \int_0^\infty \exp(-x^3) dx$$

with the relative error less than 0.02.

4.1.5 Concluding remarks

The final formulas can be written as

$$N^\infty(\infty) = f_*^\infty \Delta_\infty x (\frac{A}{2}(1 + (\frac{\Delta_\infty x}{\Delta_h x})^4)^{-1/4} + \frac{B}{2}(1 + (\frac{\Delta_\infty x}{\Delta_h x})^3)^{-1/3}) n_\infty \quad , \tag{4.1.50}$$

$$N(\infty) = \eta_{tot}(1 - \exp(-f_* \frac{n_\infty}{\eta_{tot}} (\frac{\Gamma}{4\Phi_*})^{-1/4} f_*^{-1/4} A)) \tag{4.1.51}$$

with the relative error less than the characteristic errors of the modern experiment. One can also show that the small relative error in Nz^3 can not lead to the essential errors in the final results. The spectrum of the homogeneously formed droplets is described by

$$f_{hom}(x) = f_*^\infty \exp(-\frac{\Gamma^\infty}{\Phi_*}(f_*^\infty \frac{x^4}{4} + \frac{\eta_{tot}(1 - \exp(-f_* \frac{n_\infty}{\eta_{tot}} (\frac{\Gamma}{4\Phi_*})^{-1/4} f_*^{-1/4} A))}{n_\infty} x^3)) \quad , \tag{4.1.52}$$

and the spectrum of the heterogeneously formed droplets can be presented as

$$f_{het} = f_* \exp(-\frac{\Gamma}{\Phi_*} f_* \frac{z^4}{4}) \exp(-f_* \frac{n_\infty}{\eta_{tot}} \int_0^z \exp(-\Gamma \frac{f_*}{\Phi_*} \frac{x^4}{4}) dx) \tag{4.1.53}$$

or more approximately

$$f_{het} = f_* \exp(-\frac{\Gamma}{\Phi_*} f_* \frac{z^4}{4}) \exp(-f_* \frac{n_\infty}{\eta_{tot}}(I_1 + I_2)) \quad , \tag{4.1.54}$$

where

$$I_1 = (\frac{\Gamma}{4}\frac{f_*}{\Phi*})^{-1/4}\Theta((\frac{\Gamma}{4}\frac{f_*}{\Phi*})^{1/4}z - 1)(A - \frac{\exp(-\frac{\Gamma}{4}\frac{f_*}{\Phi_*}z^4)}{4(\frac{\Gamma}{4}\frac{f_*}{\Phi*})^{3/4}z^3}) \quad , \tag{4.1.55}$$

$$I_2 = (\frac{\Gamma}{4}\frac{f_*}{\Phi*})^{-1/4}\Theta(1 - (\frac{\Gamma}{4}\frac{f_*}{\Phi*})^{1/4}z)((\frac{\Gamma f_*}{4\Phi_*})^{1/4}z - \frac{((\frac{\Gamma}{4}\frac{f_*}{\Phi*})^{1/4}z)^5}{5}) \quad . \tag{4.1.56}$$

The further evolution can be described with the help of monodisperse approximation where the total number of the droplets can be determined as $N(\infty) + N^\infty(\infty)$. This description is absolutely analogous to the homogeneous decay - the differential equation of the first order can be easily integrated.

The restriction (4.1.25) can be chancelled by the introduction in to the r.h.s. of expression for g^∞ the monodisperse approximation for the homogeneously formed droplets. Then one can came to the system of algebraic equations on $N(\infty), N^\infty(\infty)$, which can be easily solved.

We have investigated the situation $\Delta_{\zeta\eta}x < \Delta_\infty x$. If $\Delta_{\zeta\eta}x \geq \Delta_\infty x$, then $N^\infty(\infty) \ll N(\infty)$ and we come to the pure heterogeneous condensation. The value $N(\infty)$ can be calculated on the base of the known expression where we can simply neglect the homogeneous process under the vapor consumption.

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For the further analysis it is necessary to be able to describe the nucleation under the essentially nonlinear behavior of the external conditions. Here such a theory will be constructed.

4.2 Parameters of distribution in process of condensation

Again we have to formulate two statements which we have to justify analytically. The first states that the the leading role in the vapor consumption is played by the super critical embryos. The character size ρ_1

of the droplet at PIFD many times exceeds the size ρ_c of the critical embryo

$$\rho_1 \gg \rho_c \quad . \tag{4.2.1}$$

The second statement announces that the state of the near critical embryos is close to the quasi stationary one.

The second statement must be valid during PIFD. Introduce t_ζ as the characteristic time of the variation of the stationary distribution in the critical region and t_s as the time of relaxation in the near critical region. Then the required inequality can be written as

$$t_\zeta \gg t_s \quad . \tag{4.2.2}$$

These statements will be valid in the homogeneous case and in the heterogeneous case except the case when all heterogeneous centers are exhausted by the droplets. The form of the spectrum isn't important in the process of the heterogeneous formation of the droplets and later this spectrum can be considered as the monodisperse one. The second assumption can be also violated in some situations when the supersaturation is regulated only by the external conditions. Here there is no use to speak about the leading role of the droplets in the vapor consumption. In these cases the nonstationary effects due to the increase of the supersaturation and due to the decrease of the supersaturation will be approximately chancelled.

4.2.1 Homogeneous condensation

To get the form of $\zeta(x)$ it is necessary to introduce the balance equation

$$\Phi = \zeta + g \quad , \qquad g(z) = \frac{n_\infty {}_* V_*}{n_\infty V} \int_{-\infty}^{z} dx (z-x)^3 f(x) \quad . \tag{4.2.3}$$

The value t_* can be chosen as the moment of the maximum of the supersaturation. The factor $\frac{n_\infty {}_* V_*}{n_\infty V}$ is close to 1 and will be omitted.

The value of the ideal supersaturation according to the results of the second chapter can be presented in the form

$$\Phi = \Phi_* + \Phi_* (cx + lx^2)/\Gamma \tag{4.2.4}$$

with two parameters

$$c = \frac{\Gamma}{\Phi_*} \frac{d\Phi}{dx} \mid_{x=0} \quad , \quad l = \frac{\Gamma}{2\Phi_*} \frac{d^2\Phi}{dx^2} \mid_{x=0} \quad . \tag{4.2.5}$$

The negative value of l corresponds to the nonlinear character of the external conditions.

The approximation

$$f(x) = f_s \exp(\Gamma \frac{\zeta(x) - \Phi_*}{\Phi_*}) \quad , \qquad f_s = f_s(\zeta) \mid_{\zeta=\Phi_*} \tag{4.2.6}$$

is valid during PIFD.

Analyze the behavior of $g(z)$. Extract three regions. Let $l \sim 0$. Extract the period of the appearing of the main consumers of the vapor during the formation of the main quantity of the droplets. The behavior of g in the first approximation can be seen from

$$g(z) \sim \exp(z) \int_0^\infty y^3 \exp(-y) dy \quad . \tag{4.2.7}$$

One can see that

- The subintegral function in the last expression is essential only when

  $$2 \sim y_{min} \leq y \leq y_{max} \sim 4 \quad , \qquad y = c\rho \quad . \tag{4.2.8}$$

  This period corresponds to the region of the appearing of the main consumers of the vapor in the current moment of PIFD. During PIFD this region moves along ρ (and t) with the velocity of the droplets growth. When the last equations aren't valid the subintegral function is negligible. The period corresponding to (4.2.8) plays the main role in the formation of the spectrum.

Extract another two regions

- In PIFD one can extract the initial region according to

  $$-5 \leq cz \leq cz_b \quad . \tag{4.2.9}$$

  The value of z_b has to be determined with the help of the additional condition

  $$\frac{f(x) - f_1(x)}{f_1(x)} \ll 1 \quad , \tag{4.2.10}$$

  where f is the distribution of the droplets and f_1 is the imaginary distribution obtained on the base of the supersaturation Φ instead of ζ. The values in this region will be marked by the index "in".

- The estimates for $g(z)$ give the estimate from above for duration of PIFD. This period is finished when $cz \sim 1$. It starts when $cz \sim -1$. One can define the peak of PIFD according to

$$-c^{-1} < z < c^{-1} \quad . \tag{4.2.11}$$

The successful solution of the system of the condensation equations by the disballanced iterations on the second step shows that the region of the appearing of the main consumers of the vapor during PIFD lies inside the initial region. Then one can conclude that

$$-y_{min} \leq cz_b \tag{4.2.12}$$

and even

$$-y_{min} + 1 \leq cz_b \quad .$$

If $l \leq 0$ the hierarchy will be even more strong.

4.2.2 Approximation of the spectrum

It is necessary to construct some approximation for $f(x)$. Then it is necessary to get some approximation for $\zeta - \zeta_*$ in the standard approximation

$$f(x) = f_* \exp(\frac{\Gamma(\zeta - \zeta_*)}{\Phi_*}) \exp(\frac{\Gamma(\zeta_* - \Phi_*)}{\Phi_*}) \quad . \tag{4.2.13}$$

One can decompose $\zeta - \zeta_*$ into the Teilor seria in the neighborhood of $z = 0$. The expressions for the derivatives will be the following

$$\frac{d\zeta}{dz} = \frac{d\Phi}{dz} - 3\int_{-\infty}^{z} f(x)(z-x)^2 dx \quad , \tag{4.2.14}$$

$$\frac{d^2\zeta}{dz^2} = \frac{d^2\Phi}{dz^2} - 6\int_{-\infty}^{z} f(x)(z-x) dx \quad , \tag{4.2.15}$$

$$\frac{d^3\zeta}{dz^3} = \frac{d^3\Phi}{dz^3} - 6\int_{-\infty}^{z} f(x) dx \quad , \tag{4.2.16}$$

$$\frac{d^n\zeta}{dz^n} = \frac{d^n\Phi}{dz^n} - 6\frac{d^{n-4}f(z)}{dz^{n-4}} \quad , \qquad n \geq 4 \quad . \tag{4.2.17}$$

The value d^3g/dz^3 is proportional to the total number of the droplets. It is the subject of the investigation. According to the iteration procedure one can note that

- At the first step of the iterations the relative error goes to ∞.
- On the second step the characteristics are determined with a high accuracy.

So, the account of the last two expression doesn't lead to any essential influence. Then one can restrict the seria by the two first terms. This leads to the following approximation

$$f(x) = f_* \exp(\Gamma \frac{d^2\zeta}{2dz^2} \mid_{z=0} \frac{x^2}{\Phi_*}) \exp(\frac{\Gamma(\zeta_* - \Phi_*)}{\Phi_*}) \quad . \tag{4.2.18}$$

This approximation is valid only near the peak of PIFD. The standard method of the steepens descent spreads this approximation on the whole period of nucleation (including the initial region). This leads to the essential relative error. At the same time any approximation at the initial region isn't necessary because the write approximation of the spectrum here is already established

$$f(x) = f_* \exp(\Gamma \frac{\Phi(x) - \Phi_*}{\Phi_*}) \quad . \tag{4.2.19}$$

4.2.3 The equations on the parameters of the spectrum

To get the equation on the parameters of the spectrum one can differentiate the balance equations at $z = 0$ and get

$$\Phi(0) = g_{in}(0) + g_{ex}(0) + \zeta(0) \quad , \tag{4.2.20}$$

$$\frac{d\Phi}{dz} \mid_{z=0} = \{\frac{dg_{in}}{dz} + \frac{dg_{ex}}{dz} + \frac{d\zeta}{dz}\} \mid_{z=0} \quad , \tag{4.2.21}$$

$$\frac{d^2\Phi}{dz^2} \mid_{z=0} = \{\frac{d^2g_{in}}{dz^2} + \frac{d^2g_{ex}}{dz^2} + \frac{d^2\zeta}{dz^2}\} \mid_{z=0} \quad , \tag{4.2.22}$$

The indexes "in" and "ex" marks the parts of g corresponding to the droplets formed in the "initial" period and outside it. The relations (4.2.19) and (4.2.4) lead to

$$g_{in} = \sum_{i=0}^{3} z^{3-i} \alpha_i \quad , \tag{4.2.23}$$

$$\frac{dg_{in}}{dz} = \sum_{i=0}^{2} z^{2-i}(3-i)\alpha_i \quad , \tag{4.2.24}$$

$$\frac{d^2 g_{in}}{dz^2} = \sum_{i=0}^{1} z^{1-i}(3-i)(2-i)\alpha_i \quad . \tag{4.2.25}$$

In these equations α_i are defined according to

$$\alpha_i = (-1)^i \frac{3!}{i!(3-i)!} f_* \int_{-\infty}^{z_b} x^i \exp(cx + lx^2) dx \quad . \tag{4.2.26}$$

To obtain the algebraic system of equations one can substitute the integral term in the last expression by one of the Boyd estimates

$$\frac{\pi/2}{\sqrt{z^2+\pi} + (\pi-1)z} \leq \exp(z^2) \int_z^{\infty} \exp(-t^2) dt \leq \frac{\pi/2}{\sqrt{(\pi-2)z^2+\pi} + 2z} \qquad z > 0 \tag{4.2.27}$$

Analogous procedure can be applied for the values g_{ex}, $\frac{dg_{ex}}{dz}$, $\frac{d^2 g_{ex}}{dz^2}$. According to (4.2.18) the expressions for

$$g_{ex}(0) \quad dg_{ex}/dz \mid_{z=0} \quad d^2 g_{ex}/dz^2 \mid_{z=0}$$

have the following form

$$g_{ex}(0) = f_m \int_{z_b}^{0} \exp(-(\frac{x}{x_p})^2) x^3 dx = f_m x_p^4 \lambda_3 \quad , \tag{4.2.28}$$

$$\frac{dg_{ex}}{dz} \mid_{z=0} = 3 f_m \int_{z_b}^{0} \exp(-(\frac{x}{x_p})^2) x^2 dx = 3 f_m x_p^3 \lambda_2 \quad , \tag{4.2.29}$$

$$\frac{d^2 g_{ex}}{dz^2} \mid_{z=0} = 6 f_m \int_{z_b}^{0} \exp(-(\frac{x}{x_p})^2) x dx = 6 f_m x_p^2 \lambda_1 \quad , \tag{4.2.30}$$

where

$$\lambda_i = \int_{\xi_0}^{0} \xi^i \exp(-\xi^2) d\xi \quad , \quad \xi_0 = \frac{z_b}{x_p} \tag{4.2.31}$$

and x_p is some parameter like the characteristic halfwidht.

As the result one can see the system of the three algebraic equations which can be solved by the ordinary numerical methods. The solution of this equation gives all main characteristics of the process.

4.2.4 Linear source

In the case $l = 0$ the final expressions become more simple. For z_b one can take here the value $-x_p$. Then taking into account $\Gamma \gg 1$, one can obtain

$$\alpha_i = f_* \frac{3!(-1)^i}{i!(3-i)!} c^{-i-1} \sum_{j=0}^{i} \frac{i!}{(i-j)!} (-1)^j (-cx_p)^{i-j} \exp(-cx_p) \quad . \tag{4.2.32}$$

This induces the following expressions

$$g_{in}(0) = \alpha_3 = -f_* c^{-4} \sum_{j=0}^{3} \frac{3!}{(3-j)!} (-1)^j (-cx_p)^{3-j} \exp(-cx_p) \quad , \tag{4.2.33}$$

$$\frac{dg_{in}}{dz} \mid_{z=0} = \alpha_2 = f_* 3c^{-3} \sum_{j=0}^{2} (-1)^j \frac{2!}{(2-i)!} (-cx_p)^{2-j} \exp(-cx_p) \quad , \tag{4.2.34}$$

$$\frac{d^2 g_{in}}{dz^2} \mid_{z=0} = 2\alpha_1 = -f_* 6c^{-2} \sum_{j=0}^{1} (-1)^j (-cx_p)^{1-j} \exp(-cx_p) \quad . \tag{4.2.35}$$

The values of λ_i become the universal constants

$$\lambda_i = \int_{-1}^{0} \exp(-x^2) x^i dx \quad . \tag{4.2.36}$$

Introduction of the connection between $\frac{d^2\zeta}{dz^2}$ and x_p

$$\mid \frac{d^2\zeta}{dz^2} \mid = \frac{2\zeta_*}{\Gamma x_p^2} \approx \frac{2\Phi_*}{\Gamma x_p^2} \tag{4.2.37}$$

leads to the transformation from (4.2.32) - (4.2.35) to the following form

$$\Phi_* = \zeta_* - f_* c^{-4} \sum_{j=0}^{3} \frac{3!}{(3-j)!}(-1)^j(-cx_p)^{3-j}\exp(-cx_p) + f_m x_p^4 \lambda_3 \quad , \tag{4.2.38}$$

$$\frac{\Phi_* c}{\Gamma} = f_* c^{-3} 3 \sum_{j=0}^{2} \frac{2!}{(2-j)!}(-1)^j(-cx_p)^{2-j}\exp(-cx_p) + 3 f_m x_p^3 \lambda_2 \quad , \tag{4.2.39}$$

$$0 = -f_* c^{-2} 6 \sum_{j=0}^{1}(-1)^j(-cx_p)^{1-j}\exp(-cx_p) + 6 f_m x_p^2 \lambda_1 - \frac{2\Phi_*}{\Gamma x_p^2} \quad . \tag{4.2.40}$$

Then

$$f_* = \frac{\Phi_* c}{\Gamma}[c^{-3} 3 \sum_{j=0}^{2} \frac{2!}{(2-j)!}(-1)^j(-cx_p)^{2-j}\exp(-cx_p) + 3\Psi x_p^3 \lambda_2]^{-1} \quad , \tag{4.2.41}$$

where

$$\Psi = \frac{f_m}{f_*} \quad ,$$

and (4.2.40) transforms to

$$-\frac{\Phi_* c\{c^{-2} 6 \sum_{j=0}^{1}(-1)^j(-cx_p)^{1-j}\exp(-cx_p) + 6x_p^2\lambda_1\Psi\}}{\Gamma\{c^{-3}3\sum_{j=0}^{2}\frac{2!}{(2-j)!}(-1)^j(-cx_p)^{2-j}\exp(-cx_p) + 3\Psi x_p^3\lambda_2\}} = \frac{2\Phi_*}{\Gamma x_p^2} \quad . \tag{4.2.42}$$

To solve the last equation one can simplify it in the following manner: Consider Ψ as some known value. It can be found from (4.2.38). In (4.2.38), (4.2.39) in some rough approximation the last term is negligible in comparison with the second term and one can spread the approximation of the "ideal" supersaturation over this region. Then we immediately get

$$\Psi = \exp(-1) \quad .$$

Another simplification is to notice that at the characteristic scale $cx_p \sim 1$ the value of $\exp(-cx_p)$ is close to $\exp(-1)$, and linearize it near this

value. When Φ_* and Γ are given then the equation (4.2.42) for x_p is the ordinary algebraic equation of the power 4 and can be solved. Then (4.2.41) gives the value of f_m and, hence, the result for Φ_* and for Γ and completes the current step of iteration procedure for Φ_*. The structure of solution in the nonlinear case is the same one.

The system (4.2.38)-(4.2.40) allows some modifications which are available for the nonlinear case also. Note that the subintegral function $f(x)x$ in the expression for d^2g/dz^2 is essential only in the finite region of PIFD. The approximation (4.2.18) also leads to the same conclusion. Then the approximation (4.2.18) can be formally spread to the whole PIFD. Then the equation (4.2.40) leads to the following expression for x_p

$$x_p = (\frac{2\Phi_*}{3\Gamma f_m})^{1/4} \quad . \tag{4.2.43}$$

In the nonlinear case the equation (4.2.40) has the following form

$$\frac{d^2\Phi}{dz^2} = 3x_p^2 f_m - 2\frac{\Phi_*}{\Gamma x_p^2} \quad . \tag{4.2.44}$$

This bisquare equation gives the x_p dependence on f_m. Then the second equation of the system (4.2.38) - (4.2.40) becomes the closed equation on the supersaturation and can be solved by iterations. These iterations can take into account the sharp dependence of $\exp(-F_c)$ on the supersaturation. The zero approximation can be chosen as $\Gamma = 1, \Phi_* = 1$. Then the second approximation gives a rather precise result for all parameters of the spectrum. Certainly, the amplitude f_m must be obtained by the next hidden iteration instead of the explicit expression in the classical theory of nucleation.

The system of condensation equations can be even more simplified if one notices that the approximation (4.2.19) can be spread over the whole PIFD in the first and in the second equations of the system. This simplification is valid as far as the subintegral functions in the first and in the second equations are essential only in the initial region of PIFD. Finally, the system of condensation equations has the following form

$$\frac{d\Phi}{dz} \mid_{z=0} = 3f_* \int_{-\infty}^{0} x^2 \exp(cx + lx^2)dx \quad , \tag{4.2.45}$$

$$\frac{d^2\Phi}{dz^2} = 6\hat{\lambda}_1 x_p^2 f_m - 2\frac{\Phi_*}{\Gamma x_p^2} \quad , \qquad \hat{\lambda}_1 = \int_{-\infty}^{0} y \exp(-y^2)dy = 0.5 \quad . \tag{4.2.46}$$

One must take into account the difference between f_m and f_*, which is given by the first equation of the system where

$$\frac{f_*}{f_m} = \exp(-\frac{\Gamma d\Phi}{3\Phi_* dz} \mid_{z=0}$$
$$\int_{-\infty}^{0} x^3 \exp(cx + lx^2)dx / \int_{-\infty}^{0} x^2 \exp(cx + lx^2)dx) \quad . \tag{4.2.47}$$

It is essential that the equations (4.2.45) and (4.2.46) are the separate ones. The equation (4.2.45) can be solved by iterations. The total number of the droplets can be obtained as

$$N = f_m \sqrt{\pi} x_p \quad . \tag{4.2.48}$$

Ordinary the value of the parameter l is negative. But one can prove that the relative error of the last expression δ increases when l decreases in the absolute value

$$\frac{d \mid \delta \mid}{dl} > 0 \quad . \tag{4.2.49}$$

In the linear case

$$g(0) = \frac{\Phi_*}{\Gamma} \quad , \tag{4.2.50}$$

$$x_p = c^{-1}(4\exp(1))^{1/4} \quad , \tag{4.2.51}$$

$$N = \frac{\Phi_* c^3 (4\exp(1))^{1/4} \sqrt{\pi}}{6\Gamma \exp(1)} \quad . \tag{4.2.52}$$

Then N is 1.19 times greater than the result of the iteration procedure at the second step and 1.03 times greater than the result at the third step. It can be regarded as the practically precise result. All the estimates obtained for $l = 0$ remain valid in the non linear case.

When the regime of the vapor consumption differs from the free molecular one the error increases. The analogous procedure for the case of the diffusion regime of the vapor consumption gives the relative deviation between the precise solution and the mentioned procedure less than 20 percents. This case estimates the error in all possible situations from above.

The adopted approximation has some resources of the improvement inside it. Namely, it can give the value of correction term and the value

of the boundary of the region of applicability. Really, let us add the next term to the square approximation. Then we have

$$f(x) \sim f_m \exp(-(\frac{x}{x_p})^2 - (\frac{x}{x_l})^3)$$

with some parameter x_l. The value of x_l will be established from the fact that the model curve for the supersaturation

$$\zeta_{appr} = \zeta_* - \frac{\zeta_*}{\Gamma}(-(\frac{x}{x_p})^2 - (\frac{x}{x_l})^3)$$

must only touch the straight line of the ideal supersaturation at some point, which will mark the boundary between the initial region and the region of the applicability of the above given approximation.

In the case of the linear source one can get

$$x_l = (-\frac{2}{3}x_p^{-2}x_b^{-1} - \frac{1}{3}x_b^{-2})^{-1/3} \quad .$$

Having substituted this value x_l into the condition $\zeta_{appr}(x_b) = \Phi(x_b)$, one can get

$$x_b = \frac{-2 + (4 - 12x_p^{-2})^{1/2}}{2x_p^{-2}}$$

for the boundary between the initial and the central regions.

The number of the droplets must be calculated now separately over two regions.

4.2.5 Heterogeneous condensation

The straight development of the method used in the homogeneous case leads to the construction of the square approximation for the function

$$\psi = -n_\infty \int_{-\infty}^{z} dx f_* \exp(\frac{-\Gamma(\Phi_* - \zeta(x))}{\Phi_*}) + \frac{-\Gamma(\Phi_* - \zeta(z))}{\Phi_*} \quad . \quad (4.2.53)$$

The square approximation for ψ isn't suitable because the factor

$$-n_\infty \int_{-\infty}^{z} dx f_* \exp(\frac{-\Gamma(\Phi_* - \zeta(x))}{\Phi_*})$$

in the last expression has the very complicated behavior. This term goes from expression for θ. This allows to introduce the following method.

Notice that the iteration procedure in the process of the investigation of the heterogeneous condensation gives the appropriate result on the second step.

The second approximation is obtained on the base of approximation which doesn't contain any functional dependence of θ upon z. Then one can solve the pseudo homogeneous equation, i.e. the equation with $\theta = 1$ and then calculate θ according to the final step of the iteration procedure. The pseudo homogeneous equation will be solved by the method of the previous subsections. This solution will give parameters f_m, x_p. The function θ is approximately given by the following expression

$$\theta = \exp(-\Theta(z_b - z)\phi' - \Theta(z - z_b)\phi'') \quad , \tag{4.2.54}$$

where

$$\phi' = f_* n_\infty \int_{-\infty}^{z} \exp(cx + lx^2)dx \quad , \tag{4.2.55}$$

$$\phi'' = f_* n_\infty \int_{-\infty}^{z_b} \exp(cx + lx^2)dx + n_\infty f_m \int_{z_b}^{z} \exp(-(\frac{x}{x_p})^2)dx \quad . \tag{4.2.56}$$

This expression can be taken in the form of the elementary functions due to (4.2.27).

The number of the droplets which appears until $t(z)$ is obtained from θ in a very simple form

$$N(z) = \eta_{tot}(1 - \theta(z)) \quad , \tag{4.2.57}$$

based on the conservation law for the heterogeneous centers.

When the final value of θ, i.e. $\theta(\infty)$ is already obtained one can spread over the whole PIFD the approximation (4.2.18). Then the value of θ_{final} can be presented as following

$$\theta_{final} = \exp[-n_\infty f_m \sqrt{\pi} x_p] \quad , \tag{4.2.58}$$

and the total number of droplets is given by

$$N_{tot} = \eta_{tot}(1 - \exp[-n_\infty f_m \sqrt{\pi} x_p]) \quad . \tag{4.2.59}$$

The error of the above presented method is rather small as the error of the iteration procedure in the method of the disbalanced iterations. The advantage of this method lies in the fact that the iterations can't be analytically calculated in the case of the nonlinear external conditions.

Note that in the above presented procedure the cross influence of the exhausting of the heterogeneous centers can not be observed. Really, suppose that there are many heterogeneous centers of the first sort and a few centers of the other sort. In reality the second sort can not act upon the condensation of the first sort. But in final formulas the second sort acts as there is no exhausting of the second sort centers. The values Φ' and Φ'' are based on some model for the supersaturation. Only the parameter x_p is governed by the consumption of the vapor by the droplets. But it is calculated on the base of the total values of the heterogeneous centers. So, we must reconsider this procedure.

The process of exhausting of the heterogeneous centers makes the inequalities for the hierarchy of the regions more strong. So, we can repeat the above procedure with account of the exhausting of the heterogeneous centers.

For the approximation of θ_j (j marks the sort of centers) in the "initial" period one has

$$\theta_j = \exp[-\frac{f_{*\ j}}{c}\exp(cx)] \quad .$$

Then this expression must be introduced into the expressions for α_i which are the following

$$\alpha_{i\ j} = (-1)^i \frac{3!}{i!(3-i)!} f_{*j} \int_{-\infty}^{z_b} x^i \exp(cx + lx^2) \exp[-\frac{f_{*\ j}}{c}\exp(cx)]dx \quad .$$

When the last expression is going to be calculated we shall also use the steepens descent method and decompose θ into the Tailor seria near $x = z_b$.

In the zero approximation

$$\alpha_{i\ j} = (-1)^i \frac{3!}{i!(3-i)!} f_{*j} \int_{-\infty}^{z_b} x^i \exp(cx + lx^2)dx \exp[-\frac{f_{*\ j}}{c}\exp(cz_b)]$$

has the same analytical structure as in the previous case.

The further generalization is a rather simple one. We must include $\sum_j$ all times when $f_{*\ j}$. appears.

In the case of the continuous spectrum we must substitute $\sum_j$ by $\int dw$, where w is the activity of the heterogeneous center.

The alternative possibility is to consider $\exp(lx^2)$ as the correction term keeping $\exp(-\frac{f_{*\ j}}{c}\exp(cx))$ under the sign of integration.

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4.3 Kinetics of decay of metastable phase with several types of heterogeneous centers

Ordinary in the system there are the different sorts of the heterogeneous centers. In the process of the condensation on the ions the free energy depends on the sign of the electric charge. As it is shown in [64] the free energy F of an embryo in the state of internal equilibrium near the critical point can be presented in the following manner:

$$F = -b\nu + a\nu^{2/3} + c_1\nu^{1/3} + (c_2 + c_3)\nu^{-1/3} + c_0 \ln \nu - G \quad . \qquad (4.3.1)$$

Here a, b, c_0, c_1, c_2, c_3 are some constants, G is the energy of the solvatation of the heterogeneous center (the free energy is counted from this value). It necessary to notice that in contrast to a, b, c_0, c_1, c_2 which don't depend on the sign of the charge q the value of c_3 is proportional to q. The value of G also depends on the sign of q. This dependence is similar to the dependence (4.3.1) of F (without G). The only thing we must do is to substitute the number of molecules ν_e of the solvatated ion instead of ν. As far as $\nu_e \neq \nu_c$ for the near critical embryo the value of F depends on the sign of q. Hence, in presence of radiation we immediately have two types of the centers (positive and negative) with the different height of the activation barrier, i.e. with the different activity of the heterogeneous centers.

Suppose that there are several sorts of heterogeneous centers. We shall mark the total number of heterogeneous centers by $\eta_{tot\ i}$ where i marks the sort of the heterogeneous centers. The real values of the free heterogeneous centers (may be solvatated but aren't occupied by the super critical embryos) are marked by η_i. The index i or j below the value marks the sort of the heterogeneous center. The absence of this index points that the formula is valid for the arbitrary sort of the heterogeneous centers.

4.3.1 Condensation equations system

We shall mark by the argument ∞ the total values of droplets formed during the whole PIFD.

Immediately after the creation the value of the supersaturation falls to the value

$$\Phi_* = \zeta(0) - \frac{\sum_i \eta_{tot\ i}\nu_{e\ i}}{n_\infty} \quad , \qquad (4.3.2)$$

where $\nu_{e\ i}$ is the number of the condensating phase molecules in the equilibrium heterogeneous embryo. During PIFD one can assume that $\nu_{e\ i}$ is the constant value and take it at $\zeta = \Phi_*$. Ordinary $\nu_{e\ i}$ can be taken at $\zeta = \zeta(0)$.

The following statements are valid for the further consideration:

- (1) The main role in the vapor consumption during the evolution is played by the super critical embryos, i.e. by the droplets.
- (2) The quasi stationary approximation for nucleation rate is valid during PIFD.

The justification of the second statement uses the estimate for the times t_i^s of the establishing of the stationary state in the near critical region. Here it is necessary to remark that, certainly, there may exists the rather huge times t_i^s. They corresponds to the rather big values of the number of the molecules in the critical embryo. The halfwidth of the near critical region can be estimated by the homogeneous value at the supersaturation corresponding to same value of the volume of the critical embryo. It is proportional to $\nu_{c\ i}^{2/3}$. As far as the adsorption ability is proportional to $\nu_{c\ i}^{2/3}$ and the size of near-critical region is proportional to $\nu_c^{2/3}$ the value of t_i^s is proportional to $\nu_{c\ i}^{2/3}$.

In the case when $\nu_{c\ i}$ is greater than the characteristic length Δx of the size spectrum the big value of the activation barrier $\Delta F_i = F_i(\nu_{c\ i})$ ($\sim \nu_{c\ i}^{2/3}$ in the leading term) means that these sorts of the heterogeneous centers are excluded from the process. The unique situation when ΔF isn't so great occurs when the so called "macroscopic nucleus of condensation" are considered.

For the majority of the types of the heterogeneous centers the following approximations for the nucleation rates J_i are valid during the PIFD on the heterogeneous center of the given sort

$$J_i = J_i(\eta_{tot\ i}, \Phi_*) exp(\Gamma_i \frac{(\zeta - \Phi_*)}{\Phi_*}) \frac{\eta_i}{\eta_{tot\ i}} \quad , \tag{4.3.3}$$

where

$$\Gamma_i = -\Phi_* \frac{d\Delta_i F(\zeta)}{d\zeta} \mid_{\zeta=\Phi_*} \quad . \tag{4.3.4}$$

and $\Delta_i F$ is the height of the heterogeneous activation barrier. The validity of these approximations is justified for the heterogeneous embryos with the monotonous interaction between the center and the condensating phase molecules weaker or equal than the reciprocal to space distance.

One can analytically prove that the variation of the supersaturation during PIFD allows the estimate

$$\mid \zeta - \zeta_* \mid \leq \frac{\Phi_*}{\Gamma} \quad ,$$

the variation of the ideal supersaturation allows the estimate

$$\mid \Phi - \Phi_* \mid \leq \frac{\Phi_*}{\Gamma} \quad .$$

Let $f_{*\ i}$ be the amplitude value of the spectrum of the heterogeneously formed droplets measured in units of n_∞. As far as the supersaturation Φ_* and the number of the heterogeneous centers $\eta_{tot\ i}$ are the already known values it can be easily calculated by the formulas from the first chapter.

We shall mark by $n_\infty g_i$ the total number of the vapor molecules in the droplets formed on the centers of the sort "i". To simplify the formulas we shall use

$$\theta_i = \frac{\eta_i}{\eta_{tot\ i}} \quad .$$

Using the conservation laws for the heterogeneous centers and for the substance molecules we obtain for g_i, θ_i the following equations

$$g_i = f_{*\ i} \int_0^z (z-x)^3 exp(-\Gamma_i \frac{\sum_j g_j}{\Phi_*}) \theta_i dx \equiv G_i(\sum_j g_j, \theta_i) \quad , \qquad (4.3.5)$$

$$\theta_i = exp(-f_{*\ i} \frac{n_\infty}{\eta_{tot\ i}} \int_0^z exp(-\Gamma_i \frac{\sum_j g_j}{\Phi_*}) dx) \equiv S_i(\sum_j g_j) \quad , \qquad (4.3.6)$$

where $f_{*\ i} = J_i(\eta_{tot\ i}, \Phi_*)\tau / \Phi_* \alpha n_\infty$.

These equations form the closed system of equations. For simplicity we shall investigate it for $i = 1, 2$. As far as we measure the accuracy of the theory in the terms of the error of the droplets number we define these values as the following ones

$$N_i = \eta_{tot\ i}(1 - \theta_i(z)) \equiv Q_i(\theta_i) \quad . \qquad (4.3.7)$$

The spectrum of sizes can be found as the following one

$$f_i = f_{*\ i} exp(-\Gamma_i \frac{\sum_j g_j}{\Phi_*}) \theta_i \quad . \qquad (4.3.8)$$

4.3.2 Formal generalization of iteration method

The formal generalization of the iteration method leads to the following equations

$$g_{i\ (l+1)} = G_i(\sum_j g_{j\ (l)}, \theta_{i\ (l)}) \quad , \tag{4.3.9}$$

$$\theta_{i\ (l+1)} = S_i(\sum_j g_{j\ (l)}) \quad , \tag{4.3.10}$$

$$N_{i\ (l)} = Q_i(\theta_{i\ (l)}) \quad , \tag{4.3.11}$$

$$g_{i\ (0)} = 0 \quad , \tag{4.3.12}$$

$$\theta_{i\ (0)} = 1 \quad , \tag{4.3.13}$$

$$g_{i\ (1)} = f_{*\ i}\frac{z^4}{4} \quad , \tag{4.3.14}$$

$$\theta_{i\ (1)} = exp(-f_{*\ i}\frac{n_\infty}{\eta_{tot\ i}}z) \quad , \tag{4.3.15}$$

$$N_{i\ (2)}(\infty) = \eta_{tot\ i}[1 - exp(-f_{*\ i}\frac{n_\infty}{\eta_{tot\ i}}(\sum_j \frac{\Gamma_i f_{*\ j}}{4\Phi_*})^{-1/4}A)] \quad , \tag{4.3.16}$$

where

$$A = \int_0^\infty exp(-x^4)dx \approx 0.9 \quad . \tag{4.3.17}$$

Analyze the expression for $N_{i(2)}(\infty)$. Assume for a moment that for some i and j

$$f_{*\ i} \gg f_{*\ j} \quad .$$

We shall decrease $\eta_{tot\ i}$, keeping the constant value of $f_{*\ i}$, which is proportional to η_i with the fixed dependence on ζ by the increasing of activity of the heterogeneous centers of the sort "i", i.e. by the decrease of the height of the activation barrier. It is obvious that when $\eta_{tot\ i}$ is small then the total quantity of the heterogeneous centers coincides with the total number of the heterogeneously formed droplets and goes to zero when $\eta_{tot\ i}$ goes to zero. The value of g_i at the end of PIFD for heterogeneous centers of the sort "j" can be estimated as

$$g_i \leq \frac{\eta_{tot\ i}(\hat{\Delta}x_j)^3}{n_\infty} \quad ,$$

where $\hat{\Delta}x_j$ is the width of the size spectrum (the size distribution function) of the droplets of the sort "j". The value of $\hat{\Delta}x_j$ is restricted from

above by the value Δx_j, which is the width of the size spectrum without the influence of the droplets of the other sorts and the exhausting of the heterogeneous centers of this very sort. Certainly, the value of Δx_j doesn't depend on $\eta_{tot\ i}$ and on $f_{*\ i}$ for all i. Hence, the influence of the heterogeneous centers of the sort i on the process of the condensation on the centers of the sort j becomes unessential (negligible) in the limit $\eta_{tot\ i} \to 0$. At the same time the expression for $N_{j\ (2)}(\infty)$ shows that in the limit $\eta_{tot\ i} \to 0$, $f_{*\ i} = const$ the influence of the heterogeneously formed droplets of the sort i doesn't become unessential. This leads to the big error in $N_j(\infty)$. One cannot obtain the analytical expression in the third approximation for N in the frames of the standard iteration method and the second iteration gives the wrong qualitative result.

4.3.3 Limit cases

The remarkable property of the condensation in the situation considered here lies in the fact that we can construct the theory by the investigation of all limit cases and grasp practically all situations.

At first we shall extract the characteristic sizes in order to construct a rather simple solution.

Characteristic lengths

The general iteration method fails due to the inappropriate account of the cross influence of the heterogeneously droplets of the different sorts of the centers. Nevertheless it allows to define the spectrum of droplets in a write way when the cross influence is eliminated. Hence, we may use it as the characteristics of "self-formation" of the droplets of the different sorts. On the base of the first iterations in the general procedure we realize that for every separate process of the droplets formation there are two characteristic lengths. The first one is the length of the spectrum in the situation when there is no exhausting of the heterogeneous centers (and no influence of the droplets of another sort). One can say that the condensation occurs in the pseudo-homogeneous way. For this characteristic value we have:

$$\Delta_i x = (\frac{4\Phi_*}{\Gamma_i f_{*\ i}})^{1/4} \quad . \tag{4.3.18}$$

The second length is the length of the spectrum when there is no vapor exhausting but only the exhausting of the heterogeneous centers. Then

the width of the spectrum is the following

$$\delta_i x = \frac{\eta_{tot\ i}}{f_{*\ i} n_\infty} \quad . \tag{4.3.19}$$

This length is going from the first iteration for θ_i.

The hierarchy between $\Delta_i x, \delta_j x$ is ensured by the hierarchy between $f_{*\ i}, \eta_{*\ j}$. The values of Γ_i are rather (in comparison with $f_{*\ i}$) unsensitive to the variation of the supersaturation

$$-\frac{\Gamma_i}{\zeta} = \frac{d\Delta F}{d\zeta} \sim \frac{dF_c}{d\zeta} - \frac{dG}{d\zeta} \quad . \tag{4.3.20}$$

In the frames of the barrier character of condensation ($\Delta F \gg 1$), we can give the estimate from above for $(dF_c/d\zeta)$ by the value in the homogeneous condensation limit (for the short range interaction) $(dF_{c\ hom}/d\zeta)$. As far as the energy of solvatation depends on the supersaturation much more weak than $(dF_c/d\zeta)$, we can neglect the last term of the previous equation and obtain

$$\frac{d\Delta F}{d\zeta} \sim \frac{dF_{c\ hom}}{d\zeta} \quad . \tag{4.3.21}$$

But this dependence is rather weak in comparison with the very sharp dependence of $f_{*\ i}$ on the supersaturation.

Another fact to take into account is the frontal character of the back side of the spectrum in the pseudo homogeneous situation (when Γ_i plays the main role). It can be seen from

$$f_i = f_{*\ i} exp(-\frac{\Gamma_i}{4\Phi_*}(\sum_j f_{*\ j}) z^4) \quad . \tag{4.3.22}$$

Hence, the essential variation of the length $\Delta_i x$ or $\delta_i x$ can be caused only by the enormous variation of $f_{*\ i}$.

Instead of $\delta_i x$ we shall use parameter

$$h_i = \frac{\delta_i x}{\Delta_i x} \quad . \tag{4.3.23}$$

The case $\Delta_1 x \sim \Delta_2 x$

Situation $h_1 \ll 1, \quad h_2 \geq 1$

In this situation the following fact can be noticed: The process of the first sort droplets formation doesn't depend on the formation of the droplets

of the second sort. It can be directly seen from the chain of inequalities

$$\delta_1 x \ll \Delta_1 x \sim \Delta_2 x \leq \delta_2 x \quad . \tag{4.3.24}$$

So we can describe the process of the first sort droplets formation by the following equalities

$$g_1 = f_{*\ 1} \int_0^z (z-x)^3 exp(-\Gamma_1 \frac{g_1(x)}{\Phi_*}) \theta_1 dx \equiv G_1(g_1, \theta_1) \quad , \tag{4.3.25}$$

$$\theta_1 = exp(-f_{*\ 1} \frac{n_\infty}{\eta_{tot\ 1}} \int_0^z exp(-\Gamma_1 \frac{g_1(x)}{\Phi_*}) dx) \equiv S_1(g_1) \quad . \tag{4.3.26}$$

This system can be solved by iterations

$$g_{1\ (i+1)} = G_1(g_{1\ (i)}, \theta_{1\ (i)}) \quad , \tag{4.3.27}$$

$$\theta_{1\ (i+1)} = S_1(g_{1\ (i)}) \quad , \tag{4.3.28}$$

$$N_{1\ (i)} = Q_1(\theta_{1\ (i)}) \quad . \tag{4.3.29}$$

The operators G_1, S_1 and Q_1 have some remarkable properties. If for all values of arguments we have

$$w_1 \leq w_2 \quad ,$$

then

$$S_1(w_1) \leq S_1(w_2)$$

for all values of arguments. If for all values of arguments we have

$$w_1 \leq w_2 \quad ,$$

then

$$Q_1(w_1) \geq Q_1(w_2)$$

for all values of arguments. If for all values of arguments we have

$$w_1 \leq w_2 \quad ,$$

$$v_1 \geq v_2 \quad ,$$

then

$$G_1(v_1, w_1) \leq G_1(v_2, w_2)$$

for all values of arguments. Choose the initial approximations as the following ones

$$g_{1\ (0)} = 0 \quad , \tag{4.3.30}$$

$$\theta_{1\ (0)} = 1 \quad . \tag{4.3.31}$$

We see that as far as

$$g_{1\ (0)} \leq g_1 \quad ,$$

$$g_{1\ (0)} \leq g_{1\ (i)}$$

for arbitrary i, and

$$\theta_{1\ (0)} \geq \theta \quad ,$$

$$\theta_{1\ (0)} \geq \theta_{1\ (i)}$$

for arbitrary i. The following estimate is valid

$$N_{1\ (2)} \leq N_1 \leq N_{1\ (3)} \quad . \tag{4.3.32}$$

The calculation leads to

$$g_{1\ (1)} = f_{*\ 1}\frac{z^4}{4} \quad , \tag{4.3.33}$$

$$\theta_{1\ (1)} = exp(-f_{*\ 1}\frac{n_\infty}{\eta_{tot\ 1}}z) \quad , \tag{4.3.34}$$

$$N_{1\ (2)}(\infty) = \eta_{tot\ 1}(1 - exp(-f_{*\ 1}\frac{n_\infty}{\eta_{tot\ 1}}(\frac{\Gamma_1}{4\Phi_*})^{-1/4}f_{*\ 1}^{-1/4}A)) \quad . \tag{4.3.35}$$

As far as one can prove that

$$\frac{d}{dx} \mid N_{1\ (i)} - N_{1\ (j)} \mid \geq 0 \quad , \tag{4.3.36}$$

then by the numerical calculation of $N_{1(3)}(\infty)$ one can get

$$\frac{\mid N_{1\ (2)} - N_1 \mid}{N_1} \leq 0.015 \quad ,$$

which completes the iteration procedure.

On the base of iterations one can obtain some approximations for the supersaturation

$$\zeta_{(l+1)} = \Phi_* - f_{*\ 1}\int_0^z (z-x)^3 exp(-\Gamma_1\frac{g_{1\ (l)}}{\Phi_*})\theta_{1\ (l)}dx \quad . \tag{4.3.37}$$

The strong inequality allows to neglect the vapor exhausting and to obtain the second approximation for ζ

$$\zeta_{(2)} = \Phi_* - f_{*\ 1}\int_0^z (z-x)^3 exp(-Hx)dx \quad , \tag{4.3.38}$$

where

$$H = \frac{f_{*\ 1} n_\infty}{\eta_{tot\ 1}} \quad , \tag{4.3.39}$$

or after the calculation

$$\zeta_{(2)} = \Phi_* + f_{*\ 1}[-\frac{z^3}{H} + \frac{3z^2}{H^2} - \frac{6z}{H^3} + \frac{6}{H^4} - \frac{6}{H^4} exp(-Hz)] \quad . \tag{4.3.40}$$

This expression can be simplified. Let us notice that the supersaturation appears in the expression for the size spectrum $f(x)$,g,θ in the following form

$$exp(-\Gamma_i \frac{\zeta - \Phi_*}{\Phi_*}) \quad .$$

Substituting $\zeta_{(2)}$ into this expression we see that in the case when ζ essentially deviates from Φ, all terms except the first term and the second term can be neglected

$$\zeta_{(2)} = \Phi_* - z^3 \frac{\eta_{tot\ 1}}{n_\infty} \quad . \tag{4.3.41}$$

Hence, for the second sort we can obtain the following system of equations

$$g_2 = f_{*\ 2} \int_0^z (z-x)^3 exp(-\Gamma_2 \frac{g_2(x) + (\eta_{tot\ 1}/n_\infty)x^3}{\Phi_*}) \theta_2 dx \equiv G_2(g_2 + (\eta_{tot\ 1}/n_\infty)x^3, \theta_2) \tag{4.3.42}$$

and

$$\theta_2 = exp(-f_{*\ 2} \frac{n_\infty}{\eta_{tot\ 2}} \int_0^z exp(-\Gamma_2 \frac{g_2(x) + (\eta_{tot\ 1}/n_\infty)x^3}{\Phi_*}) dx) \equiv S_2(g_2 + (\eta_{tot\ 1}/n_\infty)x^3) \quad . \tag{4.3.43}$$

Having introduced

$$\lambda_2 = g_2 + (\eta_{tot\ 1}/n_\infty)z^3 \quad , \tag{4.3.44}$$

we can rewrite this system as

$$\lambda_2 = G_2(\lambda_2, \theta_2) + (\eta_{tot\ 1}/n_\infty)z^3 \equiv G_2^+(\lambda_2, \theta_2) \quad , \tag{4.3.45}$$

$$\theta_2 = S_2(\lambda_2) \quad . \tag{4.3.46}$$

The operator G_2^+ has the same properties as G_1, G_2. have. All estimates (4.3.30)-(4.3.32) remain valid after the substitution of the index "2" by "1" and the operator G^+ by G. One can get

$$\frac{d}{d(\eta_{tot\ i}/n_\infty)} \mid N_{2\ (i)} - N_{2\ (j)} \mid \leq 0 \quad , \tag{4.3.47}$$

which leads to the same estimate of the relative error (0.015) as in the pure heterogeneous condensation of the one separate sort.

The calculations according to this rather complicated procedure aren't necessary. Notice that the term $\eta_{tot\ 1} z^3/n_\infty$ initiates the characteristic length

$$D_1 = (\frac{\Phi_* n_\infty}{\Gamma_2 \eta_{tot\ 1}})^{1/3} \quad . \tag{4.3.48}$$

Really

$$D_1 \geq \epsilon \Delta_1 x \sim \epsilon \Delta_2 x \quad , \qquad \epsilon \sim (3 \pm 1) \quad . \tag{4.3.49}$$

So the condensation on the centers of the second sort occurs in the separate way and we can use the formulas (4.3.25)-(4.3.29), (4.3.33)-(4.3.36) with the substitution of the index "2" by the index "1".

Situation $h_1 \geq 1, \quad h_2 \ll 1$

As far as $\Delta_1 \sim \Delta_2$ we can change the numbers of sorts and reduce this situation to the previous one.

Situation $h_1 \geq 1, \quad h_2 \geq 1$

The exhausting of the heterogeneous centers due to $h_1 \geq 1, h_2 \geq 1$ hasn't any essential influence on the process of their formation. Hence, the cross influence is rather weak and we can use the general iteration procedure. After the calculation of iterations we have

$$g_{1\ (1)} = f_{*\ 1} \frac{z^4}{4} \quad , \tag{4.3.50}$$

$$\theta_{1\ (1)} = \exp(-f_{*\ 1} \frac{n_\infty}{\eta_{tot\ 1}} z) \quad , \tag{4.3.51}$$

$$N_{1\ (2)}(\infty) = \eta_{tot\ 1}[1 - \exp(-f_{*\ 1} \frac{n_\infty}{\eta_{tot\ 1}}((\frac{\Gamma_1}{4\Phi_*}) f_{*\ 1} + (\frac{\Gamma_1}{4\Phi_*}) f_{*\ 2}) A)^{-1/4}] \ , \tag{4.3.52}$$

$$g_{2\ (1)} = f_{*\ 2}\frac{z^4}{4} \quad , \tag{4.3.53}$$

$$\theta_{2\ (1)} = \exp(-f_{*\ 2}\frac{n_\infty}{\eta_{tot\ 2}}z) \quad , \tag{4.3.54}$$

$$N_{2\ (2)}(\infty) = \eta_{tot\ 2}[1-\exp(-f_{*\ 2}\frac{n_\infty}{\eta_{tot\ 2}}((\frac{\Gamma_2}{4\Phi_*})f_{*\ 1}+(\frac{\Gamma_2}{4\Phi_*})f_{*\ 2})^{-1/4}A)] \ . \tag{4.3.55}$$

Situation $h_1 \ll 1, h_2 \ll 1$

As far as

$$\delta_1 x \ll \Delta_1 x \sim \Delta_2 x \quad , \tag{4.3.56}$$

the droplets of the second sort don't act on the process of formation of the droplets of the first sort. Due to

$$\delta_2 x \ll \Delta_2 x \sim \Delta_1 x \tag{4.3.57}$$

the same fact is valid for the droplets of the second sort. Hence, the system is divided into pairs corresponding to the separate processes of the condensation of the different sorts. The constructions (4.3.25)-(4.3.29) can be reproduced. One can see that the cross influence can be observed due to the vapor exhausting. But in the case $h_i \ll 1$ for all i the exhausting of the vapor can be neglected in comparison with the exhausting of the heterogeneous centers.

In this situation we can obtain the precise explicit results

$$\theta_1(x) = \exp(-f_{*\ 1}\frac{n_\infty}{\eta_{tot\ 1}}z) \quad , \tag{4.3.58}$$

$$\theta_2(x) = \exp(-f_{*\ 2}\frac{n_\infty}{\eta_{tot\ 2}}z) \quad , \tag{4.3.59}$$

$$f_1(x) = f_*\exp(-f_{*\ 1}\frac{n_\infty}{\eta_{tot\ 1}}z) \quad , \tag{4.3.60}$$

$$f_2(x) = f_*\exp(-f_{*\ 2}\frac{n_\infty}{\eta_{tot\ 2}}z) \quad , \tag{4.3.61}$$

$$\zeta = \Phi_* - (\frac{\eta_{tot\ 1}}{n_\infty} + \frac{\eta_{tot\ 1}}{n_\infty})z^3 \quad . \tag{4.3.62}$$

The expression for ζ is obtained by the same procedure as that which led to (4.3.41).

Case $\Delta_1 x \ll \Delta_2 x$

The case $\Delta_2 x \ll \Delta_1 x$ is symmetric to this case and can be considered by the simple change of indexes.

Due to $\Delta_1 x \ll \Delta_2 x$ the droplets of the second sort don't act on the process of the formation of the droplets of the first sort. The formation of the droplets on the first sort of the heterogeneous centers can be described by the already described iteration procedure (relations (4.3.25)-(4.3.36)).

Situation $h_1 \ll 1, h_2 \geq 1$

Due to $h_1 \ll 1$ the equation for the first sort can be simplified and we have the following equations

$$g_1 = f_{*\ 1} \int_0^z (z-x)^3 \exp(-Hx) dx \sim \frac{\eta_{tot\ 1}}{n_\infty} z^3 \quad . \tag{4.3.63}$$

The value of θ_1 is given by (4.3.58), the value of f_1 is given by (4.3.60).

For the second sort we have equations analogous to (4.3.42),(4.3.43). So, we can adopt here the equations (4.3.44)-(4.3.47). But in this situation the inequality (4.3.49) isn't valid and we must calculate the iterations. We can choose $\lambda_{2\ (0)} = 0$ and get

$$\lambda_{2\ (1)} = f_{*\ 2} \frac{z^4}{4} + \frac{\eta_{tot\ 1}}{n_\infty} z^3 \quad , \tag{4.3.64}$$

$$\theta_{2\ (2)} = \exp(-f_{*\ 2} \frac{n_\infty}{\eta_{tot\ 2}} \int_0^z \exp(-(\frac{x}{\Delta_{\infty\ 2} x})^4 - (\frac{x}{\Delta_{h\ 1} x})^3) dx) \ , \tag{4.3.65}$$

where

$$\Delta_{\infty\ 2} x = (\frac{4\Phi_*}{\Gamma_2 f_{*\ 2}})^{1/4} \equiv \Delta_2 x$$

and

$$\Delta_{h\ 1} x = (\frac{\Phi_* n_\infty}{\Gamma_2 \eta_{tot\ 1}})^{1/3} \equiv D_1 \quad .$$

The value of $\Delta_{\infty\ 2} x$ has the sense of the spectrum width when the cross influence between centers and the exhausting of the heterogeneous centers are neglected. The value of $\Delta_{h\ 1} x$ has the sense of the spectrum width when the consumption of the vapor by the droplets is neglected.

In addition one can easily prove that

$$\frac{d}{dx} \mid N_{2\ (i)} - N_{2\ (j)} \mid \geq 0$$

and

$$\frac{d}{d\eta_{tot\ 1}} \mid N_{2\ (i)} - N_{2\ (j)} \mid \leq 0$$

for $i, j \geq 2$. It is easy to show that

$$\frac{\mid N_{2\ (2)} - N_2 \mid}{N_2} \leq 0.015 \quad ,$$

by the calculation of $N_{2\ (2)}(\infty)$ and $N_{2\ (3)}(\infty)$ at $\eta_{tot\ 1} = 0$

The analytical approximation valid for the clear interpretation can be obtained if we notice that

$$\theta_{2\ (2)}(\infty) = \exp[-f_{*\ 2}\Delta_{\infty\ 2}x\frac{n_\infty}{\eta_{tot\ 2}}(\frac{A}{2}(1 + (\frac{\Delta_{\infty\ 2}x}{\Delta_{h\ 1}x})^4)^{-1/4} + \frac{B}{2}(1 + (\frac{\Delta_{\infty\ 2}x}{\Delta_{h\ 1}x})^3)^{-1/3})] \quad , \tag{4.3.66}$$

where

$$B = \int_0^\infty \exp(-x^3)dy \quad ,$$

with the relative error less than 0.02.

The spectrum of sizes of the droplets of the second sort is the following one

$$f_2 = f_{*\ 2}\exp(-\frac{\Gamma_2 f_{*\ 2}}{\Phi_*}\frac{z^4}{4} - \frac{\Gamma_2}{\Phi_*}\frac{\eta_{tot1}}{n_\infty}z^3 - f_{*\ 2}\frac{n_\infty}{\eta_{tot\ 2}}\int_0^z \exp(-(\frac{x}{\Delta_{\infty\ 2}x})^4 - (\frac{x}{\Delta_{h\ 1}x})^3)dx) \quad . \tag{4.3.67}$$

Situation $h_1 \geq 1, h_2 \ll 1$

The description of the process of the formation of the droplets on the first sort can not be simplified. It is already fulfilled in the previous subsections. But the description of the process of the formation of the droplets on the second sort is rather simple. The supersaturation is completely determined by the condensation of the droplets on the first sort. Hence, we have the following expressions (not equations)

$$\theta_2 = \exp(-f_{*\ 2}\frac{n_\infty}{\eta_{tot\ 2}}\int_0^z \exp(-\Gamma_2\frac{g_1}{\Phi_*})dx) \quad , \tag{4.3.68}$$

$$g_2 = f_{*\,2} \int_0^z (z-x)^3 \exp(-\Gamma_2 \frac{g_1}{\Phi_*}) \theta_2 dx \quad . \tag{4.3.69}$$

The value of g_2 during the period of the nucleation on the centers of the second sort can be estimated in the following way

$$g_2 \ll \frac{\Phi_*}{\Gamma_2} \quad ,$$

which is obtained on the base of

$$\delta_2 x \ll \Delta_2 x \quad .$$

It is necessary to calculate only θ_2. To calculate θ_2 one can get into account that the value of g_1 grows so rapidly that for the value

$$\int_0^z \exp(-\Gamma_2 \frac{g_1}{\Phi_*}) dx$$

the following approximation is valid

$$\int_0^z \exp(-\Gamma_2 \frac{g_1}{\Phi_*}) dx \approx z\Theta(1 - \frac{\Gamma_2 g_1}{\Phi_*}) + \int_0^\infty \exp(-\Gamma_2 \frac{g_1}{\Phi_*}) dx \Theta(\frac{\Gamma_2 g_1}{\Phi_*} - 1) \quad ,$$

$$\int_0^z \exp(-\Gamma_2 \frac{g_1}{\Phi_*}) dx \approx z\Theta(1 - \frac{\Gamma_2 g_1}{\Phi_*}) + z_b \Theta(\frac{\Gamma_2 g_1}{\Phi_*} - 1) \quad ,$$

where z_b is extracted by the condition

$$g_1(z_b) = \frac{\Phi_*}{\Gamma_2}$$

and Θ is the Hevisaid function. The last approximation solves the problem of the analytical calculation of θ_2.

Situation $h_1 \geq 1, h_2 \geq 1$

Situation $h_1 \geq 1, h_2 \geq 1$ has been already observed in the previous subsection. Due to $\Delta_1 x \ll \Delta_2 x$ one can not consider that the inequality $h_2 \ll 1$ ensures the pure exhausting of the heterogeneous centers without the exhausting of the vapor and the consideration of the previous subsection can not be simplified.

Situation $h_1 \ll 1, h_2 \ll 1$

We have to stress that the equation $h \ll 1$ doesn't allow to say that the process of the condensation on the heterogeneous centers of the second sort is going at the constant value of the supersaturation. For the process of the condensation on the centers of the first sort we have the expressions (4.3.58), (4.3.60). The analogous expressions (4.3.59), (4.3.61) for the condensation on the centers of the the second sort can be violated. So, the process of the condensation on the centers of the second sort can not be described on the base of the unexhausted vapor.

The calculation of g_2 isn't necessary but only the calculation of θ_2 is essential. We have

$$\theta_{2\ (2)} = \exp(-f_{*\ 2}\frac{n_\infty}{\eta_{tot\ 2}}\int_0^z \exp((-(\frac{x}{\Delta_{h\ 1}x})^3)dx) \tag{4.3.70}$$

and the final value for θ_2 is

$$\theta_{2\ (2)}(\infty) = \exp[-f_{*\ 2}\Delta_{h\ 1}x\frac{n_\infty}{\eta_{tot\ 2}}B] \quad . \tag{4.3.71}$$

The monodisperse approximation is based on the evident chain

$$\hat{\Delta}x_1 \sim \delta_1 x \ll \Delta_1 x \leq \hat{\Delta}x_2 \quad .$$

We have investigated all situations. It doesn't mean that all situations can be observed in the nature. The separate consideration of the asymptote situations is necessary because later we shall assume that some weak functions of the characteristics doesn't depend on the sort of the heterogeneous centers. This assumption will be violated at the asymptotes.

4.3.4 General approximate solution

The reason why the general iteration procedure fails lies in the fact that we don't know the true expression for $g_i(z)$. In the case of the separate condensation of the different sorts we don't know this expression only when the spectrum is cut off by the exhausting of the heterogeneous centers. So, we don't know it in the situation when the converging force of the operator in the expression for θ is very strong. In the case of many sorts of the heterogeneous centers the situation is different. We don't know every term in $\sum_j g_j(z)$. Hence, we may fall in the situation when due to the first iteration the spectrum is cut off by the exhausting of

supersaturation initiated by the droplets formed on the other sort and in reality the mentioned sort of the heterogeneous centers is exhausted. So, it is necessary to invent the new more precise expression for g_i, which allows to calculate the next iteration in θ.

Monodisperse approximation

The level of the supersaturation leading to the cut off of the spectrum by the exhausting of the substance is practically one and the same for all sorts of the droplets (suppose that all Γ_i has one and the same order). Let us see the droplets of what sizes play the leading role in this cut off. Analyzing the subintergal expression in the equation for g_i, we see that this subintegral expression is a very sharp function of x. It is less than the function

$$s_{bel} = \Theta(z-x)(z-x)^3 \tag{4.3.72}$$

and greater than the function

$$s_{ab} = \Theta(z-x)(z-x)^3 \exp(-\frac{\Gamma_i \sum_j f_{*j}}{\Phi_*})\frac{x^4}{4} \quad . \tag{4.3.73}$$

Introduce the approximation for this function. One has to extract the region of the droplets sizes which are essential in the vapor consumption. This consumption is essential when

$$x \approx \Delta x \quad , \tag{4.3.74}$$

where Δx is the length of the cut off by the supersaturation. Certainly, this region must have the sizes rather small in comparison with $\Delta_i x$, because the success of the iteration procedure in the homogeneous decay on the second step of the iteration procedure is based on the fact that the droplets formed at the almost ideal supersaturation play the main role in the process of the spectrum formation. For the differential halfwidth[1] $\delta_{1/2}x$ we have the following expression

$$\delta_{1/2}x = (1 - \frac{1}{2^{1/3}})x \quad . \tag{4.3.75}$$

The integral halfwidth $\Delta_{1/2}x$ is obtained from the following equation

$$N_{ess}x^3 = f_{*\,i}\frac{x^4}{4}n_\infty \quad , \tag{4.3.76}$$

[1]It is defined as the size where the droplet contains the half of the amplitude value of the substance.

where N_{ess} is the number of the essential droplets obtained as $N_{ess} = f_{*\ i}\Delta_{1/2}xn_\infty$, which gives

$$\Delta_{1/2}x = \frac{1}{4}x \tag{4.3.77}$$

and practically coincides with $\delta_{1/2}x$. So, the subintegral function s is now divided into the essential part where

$$x \leq \frac{\Delta_i x}{4} \quad ,$$

and the tail where

$$x \geq \frac{\Delta_i x}{4} \quad .$$

We shall neglect the tail and use due to the rather small width of the essential region the monodisperse approximation for the droplets in this region. As the result we obtain the approximation for $g(x)$

$$g(z) = \frac{N(z/4)}{n_\infty} z^3 \quad , \tag{4.3.78}$$

where $N(z/4)$ is the number of the droplets appeared after $x = 0$ and until $x = z/4$. As far as the spectrum is cut off by the exhausting of the supersaturation in the frontal (sharp) manner the value of g_i is unessential before $z = \Delta_i x$ (as the small one) and after the moment of the cut off it is unessential also as there is no formation of droplets. So, instead of the previous approximation we can use

$$g_i(z) = \frac{N_i(\Delta_i x/4)}{n_\infty} z^3 \quad . \tag{4.3.79}$$

The exhaustion of the heterogeneous centers makes the subintegral function more sharp and the monodisperse approximation becomes at $\Delta_i x$ even better than in the pseudo homogeneous situation. But the exhaustion of heterogeneous centers makes the coordinate of the supersaturation cut off greater than $\Delta_i x$ and the monodisperse approximation becomes even better at the imaginary moment of the cut off of the supersaturation. Certainly, we must use $N(\Delta_i x/4)$, calculated with account of the exhaustion of heterogeneous centers.

The concluding remarks concern the fact that we can obtain $N(\Delta_i x/4)$ by the solution of the processes of the condensation for the different sorts of the centers because we need the lowest length of the cut off. This length is given without the account of the cross influence due to the frontal character of the back side of the spectrum.

Final iterations

The solution of the system of the condensation equations is given by the following procedure.

At first we must solve the equations for the separate processes

$$g_i = f_{*\ i} \int_0^z (z-x)^3 \exp(-\Gamma_i \frac{g_i}{\Phi_*})\theta_i dx \equiv G_i(g_i, \theta_i) \quad , \tag{4.3.80}$$

$$\theta_i = \exp(-f_{*\ i} \frac{n_\infty}{\eta_{tot\ i}} \int_0^z \exp(-\Gamma_i \frac{g_i}{\Phi_*})dx) \equiv S_i(g_i) \tag{4.3.81}$$

for every i.

This solution can be obtained by the known iteration procedure. The remarkable fact is that in the second approximation we can calculate the value of $\theta_{(2)}(\Delta_i x/4)$

$$\theta_{i(2)}(\Delta_i x/4) = \exp(-f_{*\ i} \frac{n_\infty}{\eta_{tot\ i}} \int_0^{\Delta_i x/4} \exp(-\frac{\Gamma_i f_{*\ i}}{4\Phi_*} z^4)dx) \quad , \tag{4.3.82}$$

$$\theta_{i(2)}(\Delta_i x/4) = \exp(-f_{*\ i} \frac{n_\infty}{\eta_{tot\ i}} (\frac{\Gamma_i f_{*\ i}}{4\Phi_*})^{-1/4} C) \quad , \tag{4.3.83}$$

where

$$C = \int_0^{1/4} \exp(-z^4)dx \approx 0.25 \tag{4.3.84}$$

and $N_{i(2)}(\Delta_i x/4)$ is given by

$$N_{i(2)}(\Delta_i x/4) = \eta_{tot\ i}(1 - \theta_{i(2)}(\Delta_i x/4)) \quad . \tag{4.3.85}$$

So, the approximations for g_i are obtained now. We must fulfill these calculations for the every sort of the heterogeneous centers.

Now we come to the common iteration procedure. The only thing we have to do is to calculate $\theta_{i\ final}$ and $N_{final\ i}(\infty)$ (these values are marked by the index "$final$"). We have obtain these values according to the iterations

$$\theta_{i\ final}(z) = \exp[-f_{*\ i} \frac{n_\infty}{\eta_{tot\ i}} \int_0^z \exp(-\frac{\sum_j \Gamma_i N_{j\ (2)}(\Delta_j x/4)}{n_\infty \Phi_*} z^3)dx] \quad , \tag{4.3.86}$$

$$N_{final\ i}(\infty) = \eta_{tot\ i}[1 - \exp(-f_{*\ i}\frac{n_\infty}{\eta_{tot\ i}}(\frac{\sum_j \Gamma_i N_{j\ (2)}(\Delta_j x/4)}{n_\infty \Phi_*})^{-1/3}B] \quad . \tag{4.3.87}$$

These expressions are valid under the reasonable split of the whole quantity of the heterogeneous centers on the different sorts of the centers. If we split formally the sort of the heterogeneous centers again and again then we shall come to the error as far as all centers will be exhausted in the initial approximation.

Suppose that the whole quantity of the heterogeneous centers of the given sort is so giant that $h_i \gg 1$. Divide this sort of the heterogeneous centers into so many subsorts that for the separate condensation on every subsort $h_{ij} \ll 1$. Moreover one can attain the situation when all imaginary subsorts are exhausted until $\Delta_i x/4$ as far as $\Delta_{ij} x$ is approximately proportional to $\eta_{ij\ tot}^{-1/4}$, (where $\eta_{ij\ tot}$ is the total number of the heterogeneous centers of the given subsort) and $\delta_{ij} x$ doesn't depend on this quantity. Then after the summation over the all subsorts we get that the number of the droplets formed on the heterogeneous centers of this sort until $\Delta_i x/4$ coincides with the total number of the heterogeneous centers of this sort (not the subsort). At the same time the cut off of the spectrum occurs due to the exhaustion of the supersaturation and it means that there are many unexhausted heterogeneous centers.

We have to correct this error. Note that the monodisperse approximation leads to some absolutely defined functional form for g and for the supersaturation.

Choose the common length Δx of the spectrum. Now the value of Δx is unknown but it satisfies to the following equation

$$\Delta x \leq \Delta_i x$$

for all sorts of the heterogeneous centers. Then one can get for g the following equation

$$g_i(z) = \frac{N_i(\Delta x/4)}{n_\infty} z^3 \quad , \tag{4.3.88}$$

which leads to the following system

$$N_{i(2)}(\Delta x/4) = \eta_{i\ tot}(1 = \theta_{i(2)}(\Delta x/4)) \quad , \tag{4.3.89}$$

$$\theta_{1(2)}(\Delta x/4) = \exp[-f_{*\ i}\int_0^z \exp(-\frac{\Gamma z^3}{\Phi_* n_\infty}\sum_j N_j(\Delta x/4))dx] \quad . \tag{4.3.90}$$

Here the weak dependence $\Gamma_i = \Gamma$ on the sort of the heterogeneous centers is neglected, but the sharp dependence f_{*j} on the sort of the heterogeneous centers is taken into account. Then one can get the following system for $N_i(\Delta x/4)$

$$N_i(\Delta x/4) = \eta_{i\ tot}(1-\exp(-f_{*\ i}\int_0^{\Delta x/4}\exp(-\frac{\Gamma}{\Phi_*}\frac{z^3}{n_\infty}\sum_j N_j(\Delta x/4))dx)) \ . \tag{4.3.91}$$

Simplify the given system. To calculate the integral one can note that

$$\int_0^x \exp(-x^3)dx \approx x \quad , \quad x \leq 1/4 \ . \tag{4.3.92}$$

Then the explicit dependence of the r.h.s. on N_j disappears. Then

$$N_i(\Delta x/4) = \eta_{i\ tot}(1-\exp(-f_{*\ i}\frac{\Delta x}{4})) \ . \tag{4.3.93}$$

Recall the sense of Δx as the halfwidth of the spectrum which is cut off by the supersaturation fall

$$\frac{\Delta x^3}{n_\infty}\sum_j N_j(\Delta x/4)\frac{\Gamma}{\Phi_*} = 1 \ . \tag{4.3.94}$$

One can get the equation on Δx

$$\frac{\Delta x^3}{n_\infty}\sum_j \eta_{j\ tot}(1-\exp(-f_{*\ j}\frac{\Delta x}{4}))\frac{\Gamma}{\Phi_*} = 1 \ . \tag{4.3.95}$$

The relation (4.3.93) expresses $N_i(\Delta x/4)$ through Δx and solves the problem.

The relation (4.3.88) gives the expression for g and for the supersaturation. The number of the heterogeneous centers is determined according to (4.3.90).

We can estimate the relative error by the pseudo homogeneous case. Then we shall obtain that the relative error can be estimated as

$$\frac{\mid N_i(\infty) - N_{final\ i}(\infty) \mid}{N_i(\infty)} \leq \frac{\mid A - B \mid}{A} \sim 0.02 \ . \tag{4.3.96}$$

The investigation of the formation of the droplets is completed.

4.3.5 Concluding remarks

The description of the further periods can be given with the help of the direct applications of the monodisperse approximation from the case of the homogeneous decay of the metastable phase. We have the equation

$$\frac{\tau}{\alpha}\frac{dz}{dt} = \zeta = \Phi_* - \sum_i N_{final\ i}(\infty)\frac{z^3}{n_\infty} \quad , \tag{4.3.97}$$

which can be easily integrated as far as the r.h.s. doesn't depend on time. So, there will be no problems in process description until the coalescence.

* * *

Such a long procedure of investigation is really necessary because in the general solution some simplifications (Γ is supposed to be constant, etc.) were used. These simplifications can not be used at the asymptotes. This leads to necessity of the separate investigation of the asymptote situations.

4.4 Kinetics of decay of metastable phase on heterogeneous centers with continuous activity

The further investigation of the heterogeneous condensation requires to take into consideration the process of the heterogeneous decay on the band of centers with the different activity. Speaking about activity of the heterogeneous centers we mean that the different activity initiates the different height of the activation barrier ΔF, i.e. the difference between the free energy of the critical embryo F_c and the free energy of solvatation G. The set of the different activities of heterogeneous centers is so dense that we can regard it as the pseudo continuous one. In the atmosphere this fact is proved experimentally. In the case of "the macroscopic nucleus of the condensation" the continuous size of the nucleus ensures the continuous set of the activities and ΔF.

4.4.1 Zeldovitch equation

We shall define the activity of the heterogeneous centers as some parameter w which is proportional to the height of the activation barrier

$$\Delta F(w) = \Delta F\ |_{w=0} - \lambda w \tag{4.4.1}$$

with some positive λ.

The total number of the heterogeneous centers with the given activity w will be marked by $\eta_{tot}(w)$. Naturally $\eta_{tot}(w)$ is a rather smooth function of w.

We must take into account the reduction of $\zeta(0)$ to some value Φ_* due to the consumption of the vapor molecules in the process of solvatation. For Φ_* we have

$$\Phi_* = \zeta(0) - \frac{\int dw \eta_{tot}(w) \nu_e(w)}{n_\infty} \quad , \tag{4.4.2}$$

where ν_e is the number of the molecules of the substance in the equilibrium embryo. The discrepancy between Φ_* and $\zeta(0)$ for the monotonous interaction between the molecules of the liquid phase and the heterogeneous center can be estimated as

$$\Phi_* - \zeta(0) \leq \eta^{tot} \frac{\nu_{c\ hom}}{n_\infty} \quad . \tag{4.4.3}$$

Here η^{tot} is the total number of the heterogeneous centers of all types

$$\eta^{tot} = \int dw \eta_{tot}(w) \quad . \tag{4.4.4}$$

The following statements are valid for the further consideration

- (1) The main role in the vapor consumption during the evolution is played by the super critical embryos, i.e. by the droplets.
- (2) The quasi stationary approximation for the nucleation rate is valid during PIFD.

The justification of the second statement uses the estimate for the times t_i^s of the establishing of the stationary state in the near critical region which can be found in the first chapter (for the heterogeneous barrier the consideration is the analogous one).

We shall mark by $n_\infty g(w)$ the total number of the vapor molecules in the droplets formed on the centers with the activity w. To simplify the formulas we shall use

$$\theta(w) = \eta(w)/\eta_{tot}(w) \quad .$$

We obtain for g, θ the following equations

$$g(z,w) = \int_0^z (z-x)^3 f_\zeta(\zeta(x), w) \eta(x,w) dx \quad , \tag{4.4.5}$$

$$\theta(z,w) = \exp(-n_\infty \int_0^z f_\zeta(\zeta(x),w)dx) \quad . \tag{4.4.6}$$

As far as we measure the accuracy of the theory in the terms of the error in the droplets number we define these values as the following ones

$$N(z,w) = \eta_{tot}(w)(1-\theta(z,w)) \equiv Q(\theta) \quad . \tag{4.4.7}$$

The total number of the droplets is

$$N^{tot} = \int \eta_{tot}(w)(1-\theta(z,w))dw = \int N(z,w)dw \quad . \tag{4.4.8}$$

For the majority of the types of the heterogeneous centers the following approximations of the nucleation rates are valid during PIFD

$$f_\zeta(\zeta(x),w) = f_\zeta(\Phi_*,w) \mid_{w=0} \exp(\Gamma\frac{(\zeta-\Phi_*)}{\Phi_*}) \exp(w\lambda) \quad , \tag{4.4.9}$$

where

$$\Gamma = -\Phi_* \frac{d\Delta_i F(\zeta)}{d\zeta} \mid_{\zeta=\Phi_*} \tag{4.4.10}$$

and ΔF is the height of the heterogeneous activation barrier. The validity of these approximations is justified for the heterogeneous embryos with the interaction between the center and the condensating phase weaker or equal than the reciprocal to the space distance. So, we can imagine this center as the hard sphere with the weak interaction on which the embryo of the pure liquid is formed.

The dependence of Γ on w is a rather weak one. So we can put

$$\Gamma(w) = \Gamma \mid_{w=0} \tag{4.4.11}$$

for some essential part of the activity spectrum.

Due to the conservation laws for the heterogeneous centers and for the molecules of the condensated substance we obtain for g, θ the following equations

$$g(z,w) = f_* \int_0^z (z-x)^3 \exp(-\Gamma\frac{g^{tot}}{\Phi_*})\theta dx \eta_{tot}(w) \exp(w\lambda) \equiv G_w(g^{tot},\theta) \quad , \tag{4.4.12}$$

$$g^{tot} = \int dw g(z,w) \quad , \tag{4.4.13}$$

$$\theta(z,w) = \exp(-f_* \exp(\lambda w) n_\infty \int_0^z \exp(-\Gamma \frac{g^{tot}}{\Phi_*}) dx) \equiv S_w(g^{tot}) \quad , \tag{4.4.14}$$

where $f_* = f_\zeta(\Phi_*, w = 0)$.

These equations form the closed system. This system will be the subject of our investigation.

The spectrum of sizes can be found as the following one

$$f(x,w) = f_* \exp(\lambda w) \exp(-\Gamma \frac{\int dw g(x,w)}{\Phi_*}) \theta(x,w) \eta_{tot}(w) \quad . \tag{4.4.15}$$

4.4.2 Iteration procedure

Such systems are ordinary solved by the iteration procedure. It can be constructed by the following way. For the initial approximations we choose

$$g_0(z,w) = 0 \quad , \qquad \theta_0 = 1 \quad . \tag{4.4.16}$$

Ordinary the recurrent procedure is defined according to

$$g_{i+1}(z,w) = G_w(g_i^{tot}, \theta_i(w)) \quad , \tag{4.4.17}$$

$$g_i^{tot}(z) = \int dw g_i(z,w) \quad , \tag{4.4.18}$$

$$\theta_{i+1}(z,w) = S_w(g_i^{tot}) \quad . \tag{4.4.19}$$

The remarkable monotonous properties of G, $\int dw$ and S ensure the estimate from above for the error of approximation. In this situation it can be observed also in the manner analogous to the case of the ordinary heterogeneous condensation. Certainly, for the calculation of the iterations we must use some expression for $\eta_{tot}(w)$. At first we shall consider the limit cases and obtain some estimates.

An interesting fact goes from the absence of η_{tot} in the r.h.s. of (4.4.19). For the rather arbitrary η_{tot} the power of exhausting will be determined only by w. The centers with the relatively small w are almost exhausted during the process of the condensation. The centers with the relatively high negative w remain unexhausted. The intermediate region has a rather small size. To give the qualitative estimates one can notice that the supersaturation ζ appears only in the function f_ζ. For the behavior of f_ζ we can obtain the following estimate

$$f_\zeta \sim f_* \exp(-const x^\epsilon) \quad , \qquad 3 \leq \epsilon \leq 4 \quad . \tag{4.4.20}$$

This estimate goes from the general obvious fact that the spectrum of the droplets must be more wide than the monodisperse one and the intensity of the formation must decrease in the x scale. So we see that the width Δx of the spectrum is the well defined value. We must stress that the last equation is valid not only for the separate condensation on the centers with the different activity but for the condensation on the centers with the set of activities.

The most rough approximation for the exhausting of the heterogeneous centers can be obtained from the first approximation of the disbalanced iteration procedure. We have

$$\theta = \exp[-f_* \exp(\lambda w) n_\infty z] \tag{4.4.21}$$

and for the final value

$$\theta_{final} = \exp[-f_* \exp(\lambda w) n_\infty \Delta x] \quad . \tag{4.4.22}$$

Define $w_<$ and $w_>$ according to the following expressions

$$w_< = w_0 - \frac{\epsilon}{\lambda} \quad , \tag{4.4.23}$$

$$w_> = w_0 + \frac{\epsilon}{\lambda} \quad , \tag{4.4.24}$$

where

$$w_0 = \frac{1}{\lambda} \ln(\frac{\ln 2}{f_* n_\infty \Delta x}) \quad , \tag{4.4.25}$$

$$\epsilon \sim 2 \; ... \; 3 \quad .$$

For $w > w_>$ almost all heterogeneous centers are exhausted. For $w < w_<$ almost all heterogeneous centers remain free. This note allows to rewrite the expression for g^{tot} in the following form

$$g^{tot} = \int_{w_<}^{w_>} dw g(z,w) + \int_{w_>}^{\infty} \eta_{tot}(w) dw \frac{z^3}{n_\infty} \quad . \tag{4.4.26}$$

The size of the intermediate region has the order of $1/\lambda$. This size corresponds to the variation of ΔF of the order of 1. As far as ΔF has the rather big values, the relative variation of ΔF in the intermediate region is rather small. So we can put in this region

$$\eta_{tot}(w) = \eta_* = const \quad . \tag{4.4.27}$$

We can spread this approximation over the region $w > w_>$ because the real activity of these centers isn't important[2]. Certainly, we must obtain the lowest boundary of this region from the following equation

$$\int_{w_>}^{w_{max}} \eta_* dw = \eta_*(w_{max} - w_>) = \int_{w_>}^{\infty} \eta_{tot}(w) dw \quad . \tag{4.4.28}$$

For $w < w_<$ any approximation is acceptable because these centers remain the free ones.

After the scale transformations $\Gamma g^{tot}/\Phi_* \to G; \quad \Gamma g/\Phi_* \to g$ we have

$$g = \frac{\Gamma f_* \eta_*}{\Phi_*} \exp(\lambda w) \int_0^z (z-x)^3 \exp(-G)\theta dx \quad , \tag{4.4.29}$$

$$G = \int_{-\infty}^{w_{max}} dw g \quad , \tag{4.4.30}$$

$$\theta = \exp[-f_* n_\infty \exp(\lambda w) \int_0^z \exp(-G) dx] \quad . \tag{4.4.31}$$

By the appropriate shift of w one can put w_{max} to zero. By the appropriate scale of w one can put λ to unity. By the appropriate choice of z we can put the coefficient in (4.4.29) to unity. As a result we have only one parameter - the coefficient in the last equation. We shall mark it by "A".

The final form of the system of the balance equations is the following one

$$g = \exp(w) \int_0^z (z-x)^3 \exp(-G)\theta dx \quad , \tag{4.4.32}$$

$$G = \int_{-\infty}^{0} dw g \quad , \tag{4.4.33}$$

$$\theta = \exp[-A \exp(w) \int_0^z \exp(-G) dx] \quad . \tag{4.4.34}$$

The iteration procedure can be constructed in the following way

$$g_{i+1} = \exp(w) \int_0^z (z-x)^3 \exp(-G_i)\theta_i dx \quad , \tag{4.4.35}$$

$$G_i = \int_{-\infty}^{0} dw g_i \quad , \tag{4.4.36}$$

[2]In the dynamic conditions the situation is the opposite and the character of the active part of the spectrum is very important.

$$\theta_{i+1} = \exp(-A\exp(w)\int_0^z \exp(-G_i)dx) \quad , \tag{4.4.37}$$

$$g_0 = 0 \quad , \quad \theta_0 = 1 \quad . \tag{4.4.38}$$

So, we have in the first iteration

$$g_1 = \exp(w)\frac{z^4}{4} \quad , \tag{4.4.39}$$

$$G_1 = \int_{-\infty}^0 dw g_1 = \frac{z^4}{4} \quad , \tag{4.4.40}$$

$$\theta_1 = \exp(-A\exp(w)z) \quad . \tag{4.4.41}$$

The second approximation gives for θ

$$\theta_2 = \exp[-A\exp(w)\int_0^z \exp(-\frac{z^4}{4})dz] \quad , \tag{4.4.42}$$

$$\theta_{final\ 2} = \exp[-A\exp(w)1.28^{1/4}] \quad . \tag{4.4.43}$$

Then for N^{tot} we have

$$N^{tot} = \int_{-\infty}^0 [1-\exp(-A\exp(w)1.28^{1/4})]dw\eta_* \quad . \tag{4.4.44}$$

For g in the second approximation we have

$$g_2 = \exp(-w)\int_0^z (z-x)^3\exp(-A\exp(w)x)\exp(x^4/4)dx \quad . \tag{4.4.45}$$

The analytical expression for these and the further iterations can not be obtained. So, we shall investigate the reduced iterations. In this procedure θ_i is substituted by θ_{i+1}. In this procedure we have

$$\theta_1 = \exp[-A\exp(w)z] \quad , \tag{4.4.46}$$

$$g_1 = \exp(w)\int_0^z (z-x)^3\exp(-A\exp(w)x)dx \quad , \tag{4.4.47}$$

$$\begin{aligned} g_1 = \frac{1}{A}z^3 - \frac{3}{A^2}z^2\exp(-w) + \frac{6}{A^3}z\exp(-2w) - \frac{6}{A^4}\exp(-3w) \\ + \frac{6}{A^4}\exp(-A\exp(w)z - 3w) \quad , \end{aligned} \tag{4.4.48}$$

$$G_1 = \int_0^z (z-x)^3 \int_{-\infty}^0 \exp(w)\exp(-A\exp(w)x)dxdw \quad , \tag{4.4.49}$$

$$G_1 = \int_0^z (z-x)^3 \frac{1}{Ax}[1-\exp(-Ax)]dx \quad . \tag{4.4.50}$$

After the decomposition of the last subintegral expression we have

$$G_1 = z^3 I_0 - 3z^2\frac{I_1}{A} + 3z\frac{I_2}{A} - \frac{I_3}{A} \quad , \tag{4.4.51}$$

where

$$I_0 = \int_0^z \frac{1}{Ax}[1-\exp(-Ax)]dx \quad , \tag{4.4.52}$$

$$I_1 = z - \frac{1-\exp(-Az)}{A} \quad , \tag{4.4.53}$$

$$I_2 = \frac{z^2}{2} + \frac{1}{A^2}Az\exp(-Az) - \frac{1}{A^2}(1-\exp(-Az)) \quad , \tag{4.4.54}$$

$$I_3 = \frac{z^3}{3} + \frac{1}{A^3}(Az)^2\exp(-Az) + \frac{2}{A^3}Az\exp(-Az) - \frac{2}{A^3}(1-\exp(-Az)) \quad . \tag{4.4.55}$$

For I_0 we have the following result

$$\int_0^z \frac{1-\exp(-y)}{y}dy = E_1(z) + \gamma + \ln(z) \quad , \tag{4.4.56}$$

where

$$\gamma = 0.57721 \quad , \qquad E_1(z) = -Ei(z) \tag{4.4.57}$$

and E_1 is the exponential integral. We can present this result in the following approximate form

$$\int_0^z \frac{1-\exp(-y)}{y}dy = z\frac{\frac{17}{3}z^2 + 60z + 480}{z^3 + 24z^2 + 180z + 480} \quad . \tag{4.4.58}$$

The final (third) approximation for θ has the following form

$$\theta_2 = \exp\{-A\exp(w)\int_0^z \exp(-G_1)dx\} \quad . \tag{4.4.59}$$

This expression can be calculated only approximately. Notice that G increases faster than x^3. The action of the subintegral factors like the

functions $\exp(-const x^n)$ at $n \geq 3$, approximately leads to the cut off of the region of the integration

$$\exp(-const x^n) \approx \Theta(const^{-1/n} - x) \quad . \tag{4.4.60}$$

In order to obtain the position of the end of the droplet formation we must solve the algebraic equation

$$G_1 = 1 \quad . \tag{4.4.61}$$

We can also use another method. From (4.4.50) after the decomposition of the exponent one can get the seria of the non-negative powers of A. So, for small A one can restrict the seria by the several first terms and promote the calculations in the following manner. All integrals with the combinations $\exp(-const x)$ and $\exp(-const x^2)$ can be calculated with the help of the Boyd approximation All terms with $\exp(-const x^n) \quad n = 3, 4, ...$ can be treated as some functions proportional to the Hevisaid function.

The value of θ_2 is the base for the final approximation for $N_{tot}(w)$. The total number of droplets can be found directly from (4.4.59) after the integration

$$N^{tot} = \eta_* \int_{-\infty}^{0} [1 - \theta(z, w) dw] \quad . \tag{4.4.62}$$

As the result we have

$$N^{tot} = \eta_* \int_{-\infty}^{0} [1 - \exp(-B \exp(-w)) dw] \quad , \tag{4.4.63}$$

where

$$B = A \int_0^z \exp(-G_1) dx \quad . \tag{4.4.64}$$

is calculated earlier. Hence, for the final expression we obtain the integral which is already calculated in (4.4.56), (4.4.58).

The alternative method is the following one. Note that in the essential region $\exp(-G_1) \leq 1$ we can decompose this exponent as function of G_1 and get the answer for $\int_0^z \exp(-G_1) dx$ in the polynomial form.

4.4.3 Universal solution method

The system of equations (4.4.32) - (4.4.34) doesn't allow the universal solution as in the case of the homogeneous condensation. Equation

(4.4.32) hasn't θ in the r.s.h.. But the operator in the r.h.s. of (4.4.32) ensures a rather rapid convergence of the iterations. The worst situation for the iteration procedure is when $A = 0$. In this situation we have the universal system

$$g = \exp(w) \int_0^z (z - x)^3 \exp(-G) dx \quad , \tag{4.4.65}$$

$$G = \int_{-\infty}^0 g dw \quad . \tag{4.4.66}$$

This system has the universal solution which will be marked by G_0. Note that the condensation process is determined by the three first momentums of the distribution function

$$\mu_i(z) = \int_0^z x^i \exp(-G)\theta dx \tag{4.4.67}$$

and by the zero momentum

$$\mu_+(z) = \int_0^z \exp(-G)\theta dx \quad , \tag{4.4.68}$$

In the pseudo homogeneous case the condensation process is determined by the analogous values which are the following ones

$$\mu_i(z) = \int_0^z x^i \exp(-G_0) dx \quad , \tag{4.4.69}$$

$$\mu_+(z) = \int_0^z \exp(-G_0) dx \quad . \tag{4.4.70}$$

After the end of the rather short period of the intensive formation we can substitute in (4.4.67) and in (4.4.68) the symbol ∞ instead of the upper limit of the integration over z. The further evolution will be determined by the four momentums $\mu_i(\infty)$ and $\mu_+(\infty)$. As far as for G we substitute the universal solution G_0 when $A = 0$ then the values of μ_i are the universal constants which can be obtained by the unique numerical solution of the last system.

We can use G_0 as the initial approximation in the iteration procedure. Then

$$\theta_1 = \exp[-A \exp(w) \int_0^z \exp(-G_0) dx] \quad , \tag{4.4.71}$$

$$g_2 = \exp(w) \int_0^z (z-x)^3 \exp(-G_0) \exp(-A \exp(w) \int_0^x \exp(-G_0) dx') dx \quad , \tag{4.4.72}$$

$$G_2 = \int_{-\infty}^0 \exp(w) \int_0^z (z-x)^3 \exp(-G_0) \exp(-A \exp(w) \int_0^x \exp(-G_0) dx') dx dw \quad . \tag{4.4.73}$$

The decomposition of the exponent gives

$$G_2 = \sum_{i=0}^{\infty} \frac{(-A)^i}{(i+1)!} P_i(z) \quad , \tag{4.4.74}$$

where

$$P_i = \int_0^z (z-x)^3 \exp(-G_0) I_{00}^i(x) dx \quad , \tag{4.4.75}$$

$$I_{00}(x) = \int_0^x \exp(-G_0) dx \quad . \tag{4.4.76}$$

Then the expression for the function B will be the following one

$$B = A \int_0^{\infty} \exp(-G_2) dx = A \int_0^{\infty} \exp(-P_0(z)) \exp(-\sum_{i=1}^{\infty} \frac{(-A)^i}{(i+1)!} P_i(z)) dz \quad . \tag{4.4.77}$$

The decomposition of the last two exponents leads to

$$B = \sum_{j=0}^{\infty} \sum_{i=0}^{\infty} \frac{(-1)^j}{j!} A \frac{(-A)^{ij}}{((i+1)!)^j} C_{ij} \quad , \tag{4.4.78}$$

where

$$C_{ij} = \int_0^{\infty} \exp(-P_0(x)) P_i^j dx \tag{4.4.79}$$

are the universal constants. For the total number of the droplets with the given activity we have

$$N_{tot}(w) = \eta_* (1 - \exp(-B \exp(w))) \quad . \tag{4.4.80}$$

For N^{tot} we repeat expressions (4.4.62), (4.4.63) with the new value of B and obtain the final result.

In the same manner one can take into account the deviation of η_* from the constant value. After the decomposition of η_* into the Tailor seria we substitute the initial approximation g_0 and act in the manner similar to (4.4.71) - (4.4.80). As a result we have some expansions in the powers of the parameter A, derivatives of η_{tot} and the universal constants.

There is another possibility to observe the universal solution in the wide class of the possible situations. We shall speak about the case of the developed spectrum of activities in the following situation. Earlier we extracted in the spectrum of the activities three regions: the region of the rather active centers (they are almost exhausted), the region of the centers with the small activity (they remain practically free during the whole process) and the intermediate region. We have noticed that in the majority of situations the intermediate region has relatively small size in comparison with the active region (the inactive region has no size - it can be spread till infinity). In this case one can fulfill some further simplifications.

Let us transmit the point $w = 0$ to the special activity for which

$$\theta \mid_{w=0} (\infty) = \frac{1}{2} \quad ,$$

i.e. the half of the centers becomes the centers of the droplets. Then the system of the condensation equations after the rescaling of w can be written as the following one

$$g = a_0 \exp(w) \int_0^z (z-x)^3 \exp(-G)\theta dx \quad , \tag{4.4.81}$$

$$G = \int_{-\infty}^{w_+} g(w)dw \quad , \tag{4.4.82}$$

$$\theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G)dx) \quad , \tag{4.4.83}$$

where w_+ is the upper boundary of the spectrum and $a_0,\ a_1$ are some constants. After the rescaling of z, x one can put $a_0 = 1$. The condition of the choice of $w = 0$ gives for a_1 the following equation

$$a_1 = \frac{\ln 2}{\int_0^\infty \exp(-G)dx} \quad . \tag{4.4.84}$$

There remains only one parameter w_+.

Now let us explicitly extract the intermediate and the active regions. One can see that for two different activities w_1 and w_2 the following equation is valid

$$\frac{\ln(\theta(w_1,x))}{\exp(w_1)} = \frac{\ln(\theta(w_2,x))}{\exp(w_2)} \quad . \tag{4.4.85}$$

The same fact is valid for the final values. The value of $\frac{\ln(\theta(w,x))}{\exp(w)}$ is invariant for the different activities in one and the same process. So, one can put $w = w_{++}$ as the boundary between these two regions, where w_{++} is equal to $2 \div 3$. In the same manner we can separate the region of inactive centers by the boundary condition $w_{--} = -w_{++}$. One can neglect the substance in the droplets on the inactive centers and get

$$G = \int_{w_{--}}^{w_+} g(w)dw \quad . \tag{4.4.86}$$

We denote by $n_\infty G_+$ the number of the molecules of the substance in the droplets formed on the active centers. The system of the condensation equations can be rewritten as

$$g = a_0 \exp(w) \int_0^z (z-x)^3 \exp(-G)dx \quad ,$$

$$G = \int_{-\infty}^{w_{++}} g(w)dw + G_+ \quad ,$$

$$\theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G)dx) \quad .$$

Now one can write the expression for G_+

$$G_+ = \frac{\eta_*}{n_\infty}(w_+ - w_{++})z^3 \quad . \tag{4.4.87}$$

The system of the condensation equations now is the following one

$$g = a_0 \exp(w) \int_0^z (z-x)^3 \exp(-G)dx \quad ,$$

$$G = \int_{-\infty}^{w_{++}} g(w)dw + \frac{\eta_*}{n_\infty}(w_+ - w_{++})z^3 \quad ,$$

$$\theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G)dx) \quad .$$

The value of w_{++} is the universal constant, but the coefficient in the term $\frac{\eta_*}{n_\infty}(w_+ - w_{++})z^3$ depends on parameters.

Defining

$$G_- = \int_{-\infty}^{w_{++}} g(w)dw \quad , \tag{4.4.88}$$

one can propose the following estimate

$$G_- \leq (w_{++} - w_{--})\frac{\eta_*}{n_\infty}z^3 \quad . \tag{4.4.89}$$

When

$$w_+ - w_{++} \gg w_{++} - w_{--} \quad ,$$

one can approximately get

$$G = \frac{\eta_*}{n_\infty}(w_+ - w_{++})z^3 \quad .$$

Then the first equation isn't necessary at all. The system looks like

$$\theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G)dx) \quad ,$$

$$G = \frac{\eta_*}{n_\infty}(w_+ - w_{++})z^3 \quad .$$

After the rescaling of x, z one can put $\frac{\eta_*}{n_\infty}(w_+ - w_{++}) = 1$ and the system looks like the universal expression

$$\theta = \exp(-\frac{\ln 2}{\int_0^\infty \exp(-z^3)dx} \exp(w) \int_0^z \exp(-z^3)dx) \quad .$$

Note that this law takes place only in the case of the developed spectrum.

Despite the rather accurate character of the methods discussed above these methods don't have the clear interpretation. That's why we pay attention to the simple method presented below. It can be applied for rather arbitrary conduction of η_{tot} as the function of w.

4.4.4 Monodisperse approximation

The level of the supersaturation leading to the cut off of the spectrum by the exhausting of the substance is practically one and the same for all sorts of droplets. Let us see the droplets of what sizes play the leading role in this cut off. Analyzing the subintegral expression in equation for

g we realize that this subintegral expression is the very sharp function of x. It is less than the function

$$s_{bel} = \Theta(z-x)(z-x)^3 \quad , \tag{4.4.90}$$

and greater than the function

$$s_{ab} = \Theta(z-x)(z-x)^3 \exp(-\frac{\Gamma \int f_* \eta_{tot}(w) \exp(\lambda w) dw}{\Phi_*} \frac{z^4}{4}) \exp(-f_* \exp(\lambda w) n_\infty z) \quad . \tag{4.4.91}$$

Let us extract the approximation for this function. We must extract the region of the droplets sizes essential in the vapor consumption during PIFD. This consumption is essential when

$$x \approx \Delta x \quad , \tag{4.4.92}$$

where Δx is the characteristic size of the cut off. This value can be introduced due to the frontal character of the back side of the spectrum. This region must have the sizes rather small in comparison with Δx, because the rapid convergence of the iteration procedure in the homogeneous decay is based on the fact that the droplets formed at the almost ideal supersaturation completely determines the process of the spectrum formation. For the differential halfwidth $\delta_{1/2}$ we have the following expression

$$\delta_{1/2} x = (1 - \frac{1}{2^{1/3}}) x \quad . \tag{4.4.93}$$

As for the integral halfwidth $\Delta_{1/2} x$ it is obtained from equation

$$N_{ess} x^3 = f_* \frac{x^4}{4} \exp(\lambda w) n_\infty \quad , \tag{4.4.94}$$

where N_{ess} is the number of the essential droplets obtained as

$$N_{ess} = f_* \exp(\lambda w) \Delta_{1/2} x n_\infty ,$$

which practically coincides with $\delta_{1/2} x$. So, the subintegral function s is now divided into the essential part where $x \leq \frac{\Delta x}{4}$, and the tail where $x \geq \frac{\Delta x}{4}$. We shall neglect the tail and use due to the rather small size of the essential region the monodisperse approximation for the droplets in this region. As the result we obtain the approximation for $g(x)$

$$g(z) = \frac{N(z/4)}{n_\infty} z^3 \quad , \tag{4.4.95}$$

where $N(z/4)$ is the number of the droplets appeared from $x = 0$ till $x = z/4$. As far as the spectrum is limited by the exhaustion of the supersaturation in the frontal (sharp) manner the value of g is unessential before $z = \Delta x$ as the small one and after the moment of the cut off it is also unessential as there is no formation of the droplets. Instead of the previous approximation we can use

$$g(z) = \frac{N(\Delta x/4)}{n_\infty} z^3 \quad . \tag{4.4.96}$$

The exhaustion of the heterogeneous centers makes the subintegral function more sharp and the monodisperse approximation becomes at Δx even better than in the pseudo homogeneous situation. But the exhausting of the heterogeneous centers makes the coordinate of the cut off by the supersaturation greater than Δx and the monodisperse approximation becomes even more better at the moment of the cut off by the supersaturation. Certainly, we must use $N(\Delta x/4)$ calculated with account of the exhaustion of the heterogeneous centers. We need the lowest length of the cut off. This length is given without the account of the cross influence due to the frontal character of the back side of the spectrum.

4.4.5 Equation on the parameters

Return to the initial system of the condensation equations and introduce the new approximation. The system of the condensation equations will be the following one

$$g = \exp(w) \int_0^z (z - x)^3 \exp(-\frac{N^{tot}(\Delta x/4)}{n_\infty} z^3) \theta dx \quad , \tag{4.4.97}$$

$$G = \int_{-\infty}^0 g dw \quad , \tag{4.4.98}$$

$$\theta = \exp[-A \exp(w) \int_0^z \exp(-\frac{N^{tot}(\Delta x/4)}{n_\infty} z^3) dx] \quad , \tag{4.4.99}$$

where

$$N^{tot}(\Delta x/4) = \int_{-\infty}^0 N_{tot}(\Delta x/4) dw \qquad N^{tot}(\Delta x/4) = \eta_{tot}(1 - \theta(\Delta x/4)) \quad . \tag{4.4.100}$$

As far as we use the monodisperse approximation we have derived the behavior of the supersaturation and need only the parameters of such behavior. We can leave the integral system and reformulate it in the terms of $N^{tot}(\Delta x/4)$. As we have seen the value of Δx is defined only by the cut off of the supersaturation. Then

$$\int_0^{\frac{\Delta x}{4}} \exp(-\frac{N^{tot}(\Delta x/4)}{n_\infty} z^3) dz = (\frac{n_\infty}{N^{tot}(\Delta x/4)})^{1/3} E \quad , \tag{4.4.101}$$

where

$$E = \int_0^{1/4} \exp(-z^3) dz \approx 0.24 \quad . \tag{4.4.102}$$

We obtain the following system

$$\theta(\Delta x/4) = \exp[-A \exp(w)(\frac{n_\infty}{N^{tot}(\Delta x/4)})^{1/3} E] \quad , \tag{4.4.103}$$

$$N^{tot}(\Delta x/4) = \int_{-\infty}^{0} dw(1 - \exp[-A \exp(w)(\frac{n_\infty}{N^{tot}(\Delta x/4)})^{1/3} E])\eta_* \quad . \tag{4.4.104}$$

The last equation is the ordinary algebraic equation with the well known methods of solution. The integral can be taken according to the procedure mentioned after (4.4.62).

When η_{tot} is some function of the activities the last equation remains the algebraic one. The number of heterogeneous centers is obtained on the base of $N^{tot}(\frac{\Delta x}{4})$ and the value of g is obtained according to (4.4.97).

4.4.6 Concluding remarks

The description of the further periods of the condensation can be given with the help of the direct application of the monodisperse approximation. We have the equation

$$\frac{\tau}{\alpha} \frac{dz}{dt} = \zeta = \Phi_* - N_r^{tot} \frac{z^3}{n_\infty} \quad , \tag{4.4.105}$$

where N_r^{tot} is the total number of the droplets. The last equation can be easily integrated as far as the r.h.s. doesn't depend on time. So, there will be no problems in the description until the coalescence.

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4.5 Heterogeneous condensation on several types of heterogeneous centers under dynamic conditions

4.5.1 The system of condensation equations

To describe the action of the external conditions introduce

$$\zeta_{id} = \frac{n_{tot}}{n_\infty} - 1 \quad .$$

Due to the solvatation the ideal supersaturation falls until

$$\Phi = \zeta_{id} - \frac{\sum_i \eta_{tot\ i} \nu_{e\ i}}{n_\infty} \quad , \tag{4.5.1}$$

where $\nu_{e\ i}$ is the number of the molecules in the equilibrium embryo.

One can approximately assume $\nu_{e\ i}$ to be constant and take it at $\zeta = \zeta_*$.

One can put

$$\Phi = \zeta_{id}$$

with the small relative error. In the further consideration we shall call Φ as the ideal supersaturation also.

To construct the model one has to prove some statements

- The main role in the vapor consumption (when it is really essential) is played by the super critical embryos.
- The quasi stationary approximation for the nucleation rate is valid during every period of the intensive formation on the every sort of the heterogeneous centers except the situations when this approximation isn't essential.

  The precise expression for the rate of nucleation is not essential in the situation of the exhausted centers (SEC). In this situation the result is obvious.
- It is possible to substitute t_* in the formalism of the iteration procedure by t_{**} which is the moment corresponding to the maximum of the supersaturation. The difference between these values becomes essential only in SEC. The parameter of the linearization of the effective ideal supersaturation can be changed.

To cancel some unimportant external parameters choose the external conditions of the constant volume and of the constant temperature of the system with some effective source of the substance.

The balance relations give for g_i, θ_i the following equations

$$g_i = f_{*\ i} \int_{-\infty}^{z_i} (z_i - x_i)^3 \exp(\Gamma_i \frac{\Phi(x) - \zeta_{*\ i}}{\zeta_{*\ i}}) \exp(-\Gamma_i \frac{\sum_j g_j}{\zeta_{*\ i}}) \theta_i dx_i \equiv G_i(\sum_j g_j, \theta_i) \quad , \tag{4.5.2}$$

$$\theta_i = \exp(-f_{*\ i} \frac{n_\infty}{\eta_{tot\ i}} \int_{-\infty}^{z_i} \exp(\Gamma_i \frac{\Phi(x) - \zeta_{*\ i}}{\zeta_{*\ i}}) \exp(-\Gamma_i \frac{\sum_j g_j}{\zeta_{*\ i}}) dx_i) \equiv S_i(\sum_j g_j) \quad , \tag{4.5.3}$$

where $f_{*\ i} = J_i(\eta_{tot\ i}, \zeta_{*\ i})\tau/\zeta_{*\ i}\alpha n_\infty$.

The system (4.5.2) - (4.5.3) is more complicate than in the case of the decay. The difficulty appears not only from the presence of $\exp(\Gamma_i \frac{\Phi(x) - \zeta_{*\ i}}{\zeta_{*\ i}})$, but also from the necessity of the introduction of the separate variables z, x for every sort of the heterogeneous centers. The periods of intensive formation of the droplets on the centers of the different sort don't coincide. This follows from the inequalities

$$\frac{f_{*\ i}}{f_{*_j}} \ll 1 \tag{4.5.4}$$

or

$$\frac{f_{*\ i}}{f_{*_j}} \gg 1 \tag{4.5.5}$$

for all arbitrary pairs of the centers i and j. The situation

$$\frac{f_{*\ i}}{f_{*_j}} \sim 1 \tag{4.5.6}$$

will be at first excluded from the consideration and later this situation will be considered.

The last two inequalities are not so sensitive to the supersaturation. Note that

$$f_* \sim \exp(-F_c + F_e) \sim \exp(-F_{c\ hom} + F_e) \quad ,$$

where the free energy F is calculated in the "absolute scale" with the zero level corresponding to the zero level in the homogeneous situation $F_{hom}(\nu = 1) = 0$. The values $F_{j\ e}$ are the free energies of the solvatation on the centers of the different sorts and we can write

$$\frac{f_{*\ i}}{f_{*_j}} \sim \frac{\eta_{i\ tot} \exp(+F_{ie})}{\eta_{j\ tot} \exp(+F_{je})} \quad . \tag{4.5.7}$$

The free energy of the solvatation isn't so sensitive to the supersaturation.

The set of the heterogeneous centers $\{\eta_{i\ tot}\}$ initiates the set of the characteristic times $\{t_{*i}\}$ and the characteristic supersaturations $\{\zeta_{i*}\}$. Suppose that $\zeta_{i\ *} > \zeta_{*\ j}$ when $i > j$.

4.5.2 External supersaturation

The analysis of the last subsection simplifies the treatment, but isn't absolutely necessary. The more rigorous recipe is to solve the separate problems

$$g_i = f_{*\ i} \int_{-\infty}^{z_i} (z_i - x_i)^3 \exp(\Gamma_i \frac{\Phi(x) - \zeta_{*\ i}}{\zeta_{*\ i}}) \exp(-\Gamma_i \frac{g_i}{\zeta_{*\ i}}) \theta_i dx_i \equiv G_i(g_i, \theta_i) \ , \tag{4.5.8}$$

$$\theta_i = \exp(-f_{*\ i} \frac{n_\infty}{\eta_{tot\ i}} \int_{-\infty}^{z_i} \exp(\Gamma_i \frac{\Phi(x) - \zeta_{*\ i}}{\zeta_{*\ i}}) \exp(-\Gamma_i \frac{g_i}{\zeta_{*\ i}}) dx_i) \equiv S_i(g_i) \ . \tag{4.5.9}$$

The solution of this problem can be obtained by the methods of the second chapter. As the result we get the set $\{\zeta_{*\ i}\}$. We can use this solution only for $i = 1$ ($\zeta_{*\ 1} < \zeta_{*\ i \neq 1}$). All other solutions are necessary only to construct the set $\{\zeta_{*\ i}\}$.

The further evolution can't be described by the system of the two last equations because the droplets formed on the centers of the first sort consume the vapor. This system must be substituted by

$$g_i = f_{*\ i} \int_{-\infty}^{z_i} (z_i - x_i)^3 \exp(\Gamma_i \frac{\Phi(x) - \zeta_{*\ i}}{\zeta_{*\ i}}) \exp(-\Gamma_i \frac{g_i + g_1}{\zeta_{*\ i}}) \theta_i dx_i \quad , \tag{4.5.10}$$

$$\theta_i = \exp(-f_{*\ i} \frac{n_\infty}{\eta_{tot\ i}} \int_{-\infty}^{z_i} \exp(\Gamma_i \frac{\Phi(x) - \zeta_{*\ i}}{\zeta_{*\ i}}) \exp(-\Gamma_i \frac{g_i + g_1}{\zeta_{*\ i}}) dx_i) \quad . \tag{4.5.11}$$

Here $i \neq 1$. In order to simplify this system it is necessary to take into account the following statement

- The spectrum of the sizes of the droplets of those sorts for which the formation of the droplets is already described can be treated as the monodisperse spectrums with some coordinates.

The solution of the system of the condensation equations was necessary to get the number of the droplets and the coordinate of the spectrum.

Then the system of equations can be reformulated as the following

$$g_i = f_{*\ i} \int_{-\infty}^{z_i} (z_i - x_i)^3 \exp(\Gamma_i \frac{\Phi(x) - \zeta_{*\ i}}{\zeta_{*\ i}}) \exp(-\Gamma_i \frac{g_i + \frac{N_{tot\ 1}}{n_\infty} z_{1\ i}^3}{\zeta_{*\ i}}) \theta_i dx_i \ , \tag{4.5.12}$$

$$\theta_i = \exp(-f_{*\ i} \frac{n_\infty}{\eta_{tot\ i}} \int_{-\infty}^{z_i} \exp(\Gamma_i \frac{\Phi(x) - \zeta_{*\ i}}{\zeta_{*\ i}}) \exp(-\Gamma_i \frac{g_i + \frac{N_{tot\ 1}}{n_\infty} z_{1\ i}^3}{\zeta_{*\ i}}) dx_i) \ . \tag{4.5.13}$$

Here $i \neq 1$, $N_{tot\ 1}$ is the total number of the droplets formed on the heterogeneous centers of the first sort and $z_{1\ i}$ is the coordinate of the spectrum of the sizes of the droplets formed on the heterogeneous centers of the first sort.

Actually

$$N_{i\ tot} \sim \eta_{i\ tot} \ .$$

If the last equality isn't valid it means that the supersaturation is going to attain the maximum and then to fall. So, no other formation of droplets can be observed.

One must solve the last system for all sorts of the heterogeneous centers to construct the sequence $\{\zeta_{*\ i}\}_{i \geq 2}$. Ordinary the sequence will be the old one, but the values are changed.

Again we can use only the lowest $\zeta_{*\ i}$, i.e. the second sort. Then we must repeat this procedure again and again. The question how to solve these systems will be discussed later.

After the condensation on i_0 sorts of the heterogeneous centers is already described and we are going to describe the condensation on the centers of sort i and the following system must be solved

$$g_i = f_{*\ i} \int_{-\infty}^{z_i} (z_i - x_i)^3 \exp(\Gamma_i \frac{\Phi(x) - \zeta_{*\ i}}{\zeta_{*\ i}}) \tag{4.5.14}$$

$$\exp(-\Gamma_i \frac{g_i + \sum_{j \le i_0} \frac{N_{tot\ j}}{n_\infty} z_{j\ i}^3}{\zeta_{*\ i}}) \theta_i dx_i \quad ,$$

$$\theta_i = \exp(-f_{*\ i} \frac{n_\infty}{\eta_{tot\ i}} \int_{-\infty}^{z_i} \exp(\Gamma_i \frac{\Phi(x) - \zeta_{*\ i}}{\zeta_{*\ i}}) \tag{4.5.15}$$

$$\exp(-\Gamma_i \frac{g_i + \sum_{j \le i_0} \frac{N_{tot\ j}}{n_\infty} z_{j\ i}^3}{\zeta_{*\ i}}) dx_i) \quad .$$

Here $i > i_0$, $N_{tot\ j}$ is the total number of droplets formed on the centers of the sort j (it is close to $\eta_{j\ tot}$), $z_{j\ i}$ is the coordinate of these droplets.

The system of the two last equations is rather complicate because the values $z_{j\ i}$ are unknown ones. The next statement simplifies the problem and reduces it to the two more simple problems

- The system of the two last equations can be with the high accuracy reduced to the following system

$$g_i = f_{*\ i} \int_{-\infty}^{z_i} (z_i - x_i)^3 \exp(\Gamma_i \frac{\Omega(x) - \Omega_{*\ i}}{\Omega_{*\ i}}) \exp(-\Gamma_i \frac{g_i}{\Omega_{*\ i}}) \theta_i dx_i \quad , \tag{4.5.16}$$

$$\theta_i = \exp(-f_{*\ i} \frac{n_\infty}{\eta_{tot\ i}} \int_{-\infty}^{z_i} \exp(\Gamma_i \frac{\Omega(x) - \Omega_{*\ i}}{\Omega_{*\ i}}) \exp(-\Gamma_i \frac{g_i}{\Omega_{*\ i}}) dx_i) \quad . \tag{4.5.17}$$

  where the function Ω satisfies the following equation

$$\Phi = \Omega + \sum_{j \le i_0} \frac{N_{j\ tot}}{n_\infty} (z + \delta z_j)^3 \quad , \tag{4.5.18}$$

$$\Omega = \frac{\tau}{\alpha} \frac{dz}{dt} \tag{4.5.19}$$

  and δz_j are some fixed and already known distances between the monodisperse spectrums.

Here the following statement is also taken into account

- The following approximation during the period of the intensive formation of the droplets on the heterogeneous centers of the given sort (PIFDGS) is valid for the nucleation rates J_i

$$J_i = J_i(\eta_{tot\ i}, \Omega_*) \exp(\Gamma_i \frac{(\zeta - \Omega_*)}{\Omega_*}) \frac{\eta_i}{\eta_{tot\ i}} \quad , \tag{4.5.20}$$

where

$$\Gamma_i = -\Omega_* \frac{d\Delta_i F(\zeta)}{d\zeta} \mid_{\zeta=\Omega_*} \quad . \tag{4.5.21}$$

The validity of the last system of the condensation equations is based on the simple fact that the rate of growth is violated by the relatively essential deviation of the supersaturation and the rate of nucleation is radically violated by the relatively small violation of the supersaturation corresponding to the moderate violation of $\frac{\Gamma_i}{\zeta}$.

We shall call Ω as the external supersaturation. Our next task is to determine it.

4.5.3 Iterations for external supersaturation

The system (4.5.18) - (4.5.19) forms the ordinary differential equation (the Abel equation) and doesn't allow the analytical solution. The initial condition is the following

$$z \mid_{t=t_{init}} = 0 \quad ,$$

where t_{init} is the time of formation of the last known peak of the droplets distribution.

Meanwhile one can construct the iterations on the base of the small parameter

$$\delta = \frac{\sum_{j \le i_0} N_{j\ tot} (z + \delta z_j)^3}{\Phi n_\infty} \quad . \tag{4.5.22}$$

We suppose that

$$\frac{d^2\Phi}{dt^2} \le 0$$

and can announce the following statements

- The iterations defined according to

$$\Phi = \frac{\tau}{\alpha} \frac{dz_{(k+1)}}{dt} + \sum_{j \le i_0} \frac{N_{j\ tot}}{n_\infty} (z_{(k)} + \delta z_j)^3$$

converge to a unique solution (an ordinary property of the differential equation)[3].

[3] Assume $z_{(0)} = 0$.

- We need to investigate the region where

$$\frac{d\Omega}{dt} \geq 0 \quad .$$

When $\frac{d\Omega}{dt} = 0$ at the final of the period then we have

$$\frac{d(z_{(k)} - z_{(k+1)})}{d(\frac{d^2\Phi}{dt^2})} \geq 0 \quad .$$

We can shift t_{init} to the time of formation of the first peak and consider all δz_j as some positive values. Then

$$\frac{d(z_{(k)} - z_{(k+1)})}{d\delta z_j} \leq 0 \quad .$$

The last inequality in the mentioned reformulation can be also applied. We can put t_{init} to the moment when $\Phi = 0$ and consider some positive shifts z_j. Then the other inequality can be taken into account

$$\frac{d(z_{(k)} - z_{(k+1)})}{dt_{init}} \geq 0 \quad .$$

It is obvious that t_{init} can not be earlier than the moment when $\Phi = 0$.

In the worst situation the form of the differential equation is the following

$$At = \frac{\tau}{\alpha}\frac{dz}{dt} + \frac{N_{tot}}{n_\infty}z^3 \quad , \tag{4.5.23}$$

where A and N_{tot} are some constants.

If Φ is the polynomial then all iterations are calculated analytically and have the form of polynomials. Their convergence is rather high. The value of the relative error in the maximum of Ω

$$\Delta_i \leq \frac{|max_t\Omega_{(i)} - max_t\Omega|}{max_t\Omega}$$

is less than

$$\Delta_{i\ i+1} \sim \frac{|max_t\Omega_{(i)} - max_t\Omega_{(i+1)}|}{max_t\Omega_{(i+1)}} \quad .$$

and can be easily calculated on the base of (4.5.23). As a result one can get $\Delta_2 < 4.2 * 10^{-2}$, $\Delta_3 < 8.68 * 10^{-3}$.

Note that the requirement for the choice of the number of iterations is the following

$$\Delta_k \leq \frac{1}{\Gamma_i} \quad .$$

Really, Γ_i is the big parameter of the theory and goes to infinity, but actually at least $\Gamma_i \sim 50$ which is necessary for the rather intensive formation of the droplets ($f_* \sim \exp(-const\Gamma_i^{2/3})$). It is necessary to calculate only the few first iterations.

One can introduce the other more accurate approximation - the approximation of the ideal surface. In this approximation the term Dz^3 is divided between the surface term z^2 and the linear term z. The iterations are constructed by the following way

$$\Phi = \frac{\tau}{\alpha}\frac{dz_{(k+1)}}{dt} + \sum_{j \leq i_0} \frac{N_{j\ tot}}{n_\infty}(z_{(k)} + \delta z_j)^2(z_{(k+1)} + \delta z_j) \quad .$$

4.5.4 Formation of the droplets

Now we are going to solve the system (4.5.16) - (4.5.17). It is impossible to linearize Ω as the function of time and of x during PIFDGS. But some important conclusions about the behavior of Ω can be made. Consider the given sort of the heterogeneous centers i on which the droplets are already formed. Introduce the characteristic width Δx of the peak which is going to be formed. Certainly,

$$\Delta x \ll z_i \quad . \tag{4.5.24}$$

The value of g_i near $z \sim 0$ allows to give the estimate

$$g_i \sim \frac{N_{i\ tot}}{n_\infty} z_i^3 \quad .$$

We can also give the analogous estimates for the derivatives

$$\frac{dg_i}{dz} \sim \frac{N_{i\ tot}}{n_\infty} z_i^2 \quad ,$$

$$\frac{d^2 g_i}{dz^2} \sim \frac{N_{i\ tot}}{n_\infty} z_i \quad ,$$

$$\frac{d^3 g_i}{dz^3} \sim \frac{N_{i\ tot}}{n_\infty} \quad .$$

The actions of this terms on Ω are given by the following expressions

$$\frac{dg_i}{dz} \to \frac{N_{i\ tot}}{n_\infty} z_i^2 \Delta x \quad ,$$

$$\frac{d^2 g_i}{dz^2} \to \frac{N_{i\ tot}}{n_\infty} z_i (\Delta x)^2 \quad ,$$

$$\frac{d^3 g_i}{dz^3} \to \frac{N_{i\ tot}}{n_\infty} (\Delta x)^3 \quad .$$

Due to (4.5.24) one can see that

$$\frac{N_{i\ tot}}{n_\infty} z_i^2 \Delta x \gg \frac{N_{i\ tot}}{n_\infty} z_i (\Delta x)^2 \gg \frac{N_{i\ tot}}{n_\infty} (\Delta x)^3 \quad .$$

The action of $\frac{dg_i}{dt}$ can be canceled by $\frac{d\Phi}{dt}$ because they have the different signs. Then the action of $\frac{d^2 g_i}{dt^2}$. must be taken into account. The action of $\frac{d^3 g_i}{dt^3}$ can be neglected.

As the result we justify the following approximation of Ω during PIFDGS:

$$\Omega = cx + lx^2 \quad , \tag{4.5.25}$$

with two constants.

The characteristic length of the formation of the spectrum by the vapor consumption of the peak under formation is given by the following formula

$$\Delta x \sim (\frac{\Omega_i}{\Gamma_{i\ *} f_{*\ i}})^{1/4} \quad .$$

The halfwidth of the spectrum initiated by the external supersaturation is given by

$$x_p = (\frac{2\Omega_{max}}{\Gamma_i \frac{d^2\Omega}{dx^2}\ |_{max}})^{1/2} \quad ,$$

when the formation of the droplets occurs near the maximum of Ω.

When $\Delta_x \ll x_p$, we can use the disbalanced iterations procedure. When $\Delta x \gg x_p$ or $\Delta x \sim x_p$ one can use the modified method of the steepens descent which is constructed in this chapter. The case $\Delta x \gg x_p$ is very simple (ζ coincides with Ω). The modified method of the steepens descent is valid for all situations described here.

4.5.5 Final remarks

The applicability of the quasi stationary distribution function as the boundary condition for kinetic equation is based on the fact that the characteristic time of the establishing of the stationary distribution in the region $\nu^{1/3} \leq 3\nu_c^{1/3}$ is negligible in comparison with the characteristic time of the variation of the supersaturation up to the value ζ/Γ_i. This statement is valid in all situations except the situations when there occurs the total exhausting of heterogeneous centers and the result is the obvious one - all centers of the given sort became the centers of the droplets. This fact can be proved analytically. Also one can prove that the main consumers of the vapor are the super critical embryos, i.e. the droplets.

The quasistationarity can be also violated when $\Delta x \gg x_p$. One can show that in this case the effects of the non stationarity are approximately canceled.

Consider how one can include the situation (4.5.6) in the general consideration. Note that in the iteration procedure as far as in the modified method of the steepens descent the final expressions for θ and N are given on the base of approximations obtained from the "ideal" laws. In the "ideal" laws the analytical structure of the expressions for the different sorts of centers is one and the same. Then the generalization is rather simple. It is necessary to choose the common coordinates x, z and to calculate directly the iterations (or to use the modified method of the steepens descent). For $\theta_{(2)\ i}$ one can get the separate expressions

$$\theta_{(2)\ i} = \exp(-f_{*\ i}\frac{n_\infty}{\eta_{i\ tot}}\frac{c^3\Omega_*}{6\Gamma_i(f_{*\ i}+f_{*\ j})}$$

$$(1-\exp(-\frac{6\Gamma_i(f_{*\ i}+f_{*\ j})}{c^4\Omega_*}\exp(cz)))) \quad .$$

There is no cross effect of the exhaustion of the heterogeneous centers. To see this effect one can use the modified method of the steepens descent. This effect is rather weak.

The account of the nonisothermal effects is rather simple. The variation of the rate of nucleation leads to the variation of the stationary distribution in $\frac{\zeta+1}{\zeta}\ln(\zeta+1)$ times (i.e. the renormalization has the constant value). Then the process can be described by the effective account that in the condensation of one molecule the droplet effectively accumulates (k_2+1) molecules, where k_2 is some fixed known parameter [40]. The description is reduced to the clear renormalizations.

The global evolution of the system doesn't allow the constant renormalization. But one can show that the generalization of the iteration procedure mentioned in this chapter (where $\frac{dz}{dt}$ is unknown) leads to the rather precise description. The initial approximation in this procedure has to be taken as the solution obtained on the base of the constant rescaling. The application of this procedure allows to overcome the restriction $k_2 \gg 1$ from [40] for the condensation on the one sort of the heterogeneous centers.

4.6 Kinetics of condensation on centers with continuous activity under dynamic conditions

4.6.1 The system of the condensation equations

Denote by the argument ∞ the total quantities of the values formed during the whole process of the condensation.

The value of η^{tot} will mark the total centers of all types

$$\eta^{tot} = \int dw \eta_{tot}(w) \quad , \tag{4.6.1}$$

where $\eta_{tot}(w)$ is the total number of the heterogeneous centers of the given type (the density on the activity of the total number of the heterogeneous centers).

The following statements will be valid in the further consideration

- The main role in the vapor consumption is played by the droplets, i.e. by the super critical embryos.
- The quasi stationary approximation for the rate of the nucleation is valid during PIFD for those sorts of the heterogeneous centers which are not completely exhausted in this process.

Denote by $n_\infty g(w)$ the distribution on activity of the total numbers of the substance in the droplets with activity w. To simplify the formulas we use

$$\theta(w) = \eta(w)/\eta_{tot}(w) \quad .$$

We can get for g_i, θ_i the following equations

$$g(z,w) = \int_{-\infty}^{z} (z-x)^3 f_\zeta(\zeta(x),w)\eta(w)dx \quad , \tag{4.6.2}$$

$$\theta(z,w) = \exp(-n_\infty \int_{-\infty}^{z} f_\zeta(\zeta(x),w)dx) \quad . \tag{4.6.3}$$

As far as we estimate the accuracy of the theory by the error in the total number of the droplets we have to determine these values

$$N(z,w) = \eta_{tot}(w)(1-\theta(z,w)) \equiv Q(\theta) \quad . \tag{4.6.4}$$

The total number of the droplets is determined as

$$N^{tot} = \int \eta_{tot}(w)(1-\theta(z,w))dw = \int N(z,w)dw \quad . \tag{4.6.5}$$

For the majority of the types of the heterogeneous centers the following approximation for the nucleation rate

$$f_\zeta(\zeta(x),w) = f_\zeta(\Phi_*,w) \mid_{w=0} \exp(\Gamma\frac{(\zeta-\Phi_*)}{\Phi_*})\exp(w\lambda) \equiv$$
$$f_{\zeta\ *}\exp(\Gamma\frac{(\zeta-\Phi_*)}{\Phi_*})\exp(w\lambda) \tag{4.6.6}$$

is valid during PIFD. Here

$$\Gamma = -\Phi_* \frac{d\Delta F(\zeta)}{d\zeta} \mid_{\zeta=\Phi_*}\mid_{w=0} \quad , \tag{4.6.7}$$

$$f_{\zeta\ *} = f_\zeta(\Phi_*,w) \mid_{w=0}$$

and ΔF is the height of the heterogeneous activation barrier. The validity of these approximations is justified for the heterogeneous embryos with the interaction between the center and the condensating phase molecules weaker or equal than the reciprocal to the space distance. We can imagine the nuclei as the hard sphere with the weak interaction on which the embryo of the pure liquid is formed.

The dependence of Γ on w is the rather weak one. We can put

$$\Gamma(w) = \Gamma \mid_{w=0} \tag{4.6.8}$$

for some essential part of the activity spectrum. The applicability of the last approximation is based on the following model. It is known

that Γ is approximately $\nu_e - \nu_c$. Under the essential variation of the supersaturation the value of ν_e doesn't have some big variations and the variation of Γ occurs mainly due to the variation of ν_c. The behavior of the value of ν_c resembles the behavior in the homogeneous case. As a result we can justify not only the approximation of the dependence on the supersaturation, but also the dependence on activity.

One has to extract the essential part of the spectrum. The process of the condensation on the centers with the relatively high activity occurs earlier than the supersaturation attains maximum. These centers form the droplets which can be included in the value of external supersaturation. For these centers the number of the formed droplets approximately coincides with the number of the centers - all centers are the centers of the droplets.

The action of this part of the spectrum on the further evolution can be treated in the terms of the external supersaturation Ω. The nontrivial statement is that the process of the formation of the droplets on the centers with the intermediate activity occurs near the maximum of the supersaturation This statement lies in the base of this method of description. This fact can be also analytically proved.

The centers with the relatively low activity remains practically unexhausted (if the spectrum η_{tot} has no singularities). The singularities can be described in this region by the manner from the previous section.

Only some intermediate centers are essential near the maximum of the supersaturation. In the scale of activity this region corresponds to the variation of w by the value of the order λ^{-1}.

Now we shall come to the system of the balance equations for the functions $g(x,w)$, $\theta(x,w)$ and

$$G(x) = \int dw g(x,w) \quad ,$$

where the integral is taken over the whole spectrum of the heterogeneous centers. We can write that the region of the integration goes from $-\infty$ up to ∞, but in fact this integration must be carried out in the region covering the essential region of the spectrum. In this region it is necessary to have the relatively smooth behavior of η_{tot}. This value must be approximately constant

$$\eta_{tot} \approx const$$

or must be well approximated by the polynomial on activity

$$\eta_{tot} = P_n(w) \quad .$$

Using the conservation laws for the heterogeneous centers and for the substance we get for g, θ the following equations

$$g(z,w) = f_* \int_{-\infty}^{z} (z-x)^3 \exp(-\Gamma \frac{\zeta - \Phi_*}{\Phi_*}) \theta dx \exp(w\lambda) \quad , \tag{4.6.9}$$

$$G(z) = \int dw g(z,w) \quad , \tag{4.6.10}$$

$$\theta(z,w) = \exp(-\frac{f_* \exp(\lambda w) n_\infty}{\eta_{tot}} \int_{-\infty}^{z} \exp(-\Gamma \frac{\zeta - \Phi_*}{\Phi_*}) dx) \quad , \tag{4.6.11}$$

$$\Phi = \zeta + G(z) \quad , \tag{4.6.12}$$

where $f_* = f_{\zeta\ *} \eta_{tot}$.

These equations form the closed system of the condensation equations.

We shall investigate this system during the period when the centers with intermediate activity are going to become the centers of the droplets. We shall also call this period as PIFD.

We assume that the ordinary linearization of the ideal supersaturation is valid during PIFD

$$\Phi(x) = \Phi_* + \frac{\Phi_*}{\Gamma} cx \tag{4.6.13}$$

with some parameter c.

After the substitution of this linearization into the system of the condensation equations this system transfers to

$$g(z,w) = f_* \int_{-\infty}^{z} (z-x)^3 \exp(cx - \frac{\Gamma}{\Phi_*} G(x)) \theta(x,w) dx \exp(w\lambda) \quad , \tag{4.6.14}$$

$$G(z) = \int dw g(z,w) \quad , \tag{4.6.15}$$

$$\theta(z,w) = \exp(-\frac{f_* \exp(\lambda w) n_\infty}{\eta_{tot}} \int_{-\infty}^{z} \exp(cx - \frac{\Gamma}{\Phi_*} G(x)) dx) \quad . \tag{4.6.16}$$

The spectrum of sizes can be found as the following one

$$f(x,w) = f_* \exp(\lambda w) \exp(-\Gamma \frac{\zeta - \Phi_*}{\Phi_*}) \theta(x,w) \tag{4.6.17}$$

and when the linearization is taken into account:

$$f(x,w) = f_* \exp(\lambda w) \exp(cx - \frac{\Gamma}{\Phi_*} G(x)) \theta(x,w) \quad . \tag{4.6.18}$$

4.6.2 Iteration procedure

The iterations to solve the problem is constructed by the following way. For the initial approximations we choose

$$g_0(z,w) = 0 \quad , \qquad \theta_0(z,w) = 1 \quad . \tag{4.6.19}$$

The recurrent procedure is defined according to

$$g_{i+1}(z,w) = f_* \int_{-\infty}^{z} (z-x)^3 \exp(cx - \frac{\Gamma}{\Phi_*} G_i(x)) \theta_i(x,w) dx \exp(w\lambda) \quad , \tag{4.6.20}$$

$$G_i(z) = \int dw g_i(z,w) \quad , \tag{4.6.21}$$

$$\theta_{i+1}(z,w) = \exp(-\frac{f_* \exp(\lambda w) n_\infty}{\eta_{tot}} \int_{-\infty}^{z} \exp(cx - \frac{\Gamma}{\Phi_*} G_i(x)) dx) \quad . \tag{4.6.22}$$

The well known chains of the inequalities guarantees the estimates analogous to the already obtained in the second chapter.

The direct calculation of iterations gives

$$g_1(z,w) = f_* \frac{6 \exp(cz)}{c^4} \exp(\lambda w) \quad , \tag{4.6.23}$$

$$\theta_1(x,w) = \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w) \frac{\exp(cx)}{c}) \quad , \tag{4.6.24}$$

$$G_1(x) = f_{\zeta\ *} \frac{6 \exp(cx)}{c^4} \int dw \exp(\lambda w) \eta_{tot} \quad . \tag{4.6.25}$$

The last integral causes some problems with convergence. When $\eta_{tot} = const$ it can not be calculated. At least there are two possibilities.

The first possibility is the more formal one. Certainly, in every system $\eta_{tot}(w) = 0$ when w is greater than some maximum value w_{max}. So formally the integral exists and it is equal to some constant. This constant is the generally unknown one, but one can act in the manner like it was done with the supersaturation in the method of the disbalanced iterations. In the disbalanced iterations the value of Φ_* was not the matter of consideration but was included in the set of the undetermined parameters. After the final form of the size spectrum was already established the equation on parameters was formulated. The form of the spectrum played a role of some ansatz with the several parameters. The same procedure can be implemented here.

The reason is that we can observe the separation of the functions containing w from the terms containing the other parameters of the condensation. This fact remains valid in the second iteration which seems to be the rather good approximation for the final solution. One can call this phenomena as the "approximate separation of activities".

The second possibility seems to be the more physical one because it allows to combine the current problem with the problem of the correct definition of the region of the rather active centers and the region of the exhausted centers. We have not separated the region included into the external supersaturation from the region which isn't included into the external supersaturation. Note, that in the dynamic conditions the spectrum of sizes of the droplets formed on the fixed sort of the heterogeneous centers has the well defined boundaries. The sizes (and the times of formation) of the droplets essential in the vapor consumption can be also well localized. Namely, the spectrum is essentially situated in the region

$$-\frac{1}{c} \leq z \leq \frac{1}{c} \tag{4.6.26}$$

and the region of the droplets which are essential for the vapor consumption during PIFD is covered by the interval

$$-\frac{5}{c} \leq z \leq 0 \quad . \tag{4.6.27}$$

As a result one can say that for $z \sim -a/c$ where $a \sim 5$, one can determine the start of PIFD for centers which are essential in the process of nucleation near the maximum of the supersaturation.

The moment t_* can be taken as a moment of the maximum of the supersaturation. Really, when the maximum of the intensity of formation (or the formation of the half of the droplets) lies far from maximum of the supersaturation then the result of the nucleation of this sort of centers is rather obvious: the supersaturation is equal to the ideal (or to the external) supersaturation

$$\zeta = \Phi \quad ,$$

the total number of the droplets is equal to the total number of centers

$$N_{tot} = \eta_{tot}$$

and the moment of the formation of the spectrum which can be considered as monodisperse one can be found from

$$f_{\zeta\,*} \exp(\lambda w) n_\infty = c \ln 2 \quad ,$$

where the first two terms can be changed by some other amplitude of the spectrum. The parameter c can be reconsidered as far as the derivative can vary.

The simplest regularization by the cut off is the following one. We must substitute the value of η_{tot} by the value η_{init}, calculated as

$$\eta_{init} = \eta_{tot}\theta(x = -a, w)$$

after the calculation of $\theta(-a, w)$ which can be calculated on the base of the ideal supersaturation, i.e. in the first iteration. As far as

$$\theta_1(-a, w) = \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w)\frac{\exp(-ca)}{c}) \quad ,$$

the value of f_* must be changed by

$$f_* = f_{\zeta\ *}\eta_{tot}(w)\exp(-f_{\zeta\ *} n_\infty \exp(\lambda w)\frac{\exp(-ca)}{c}) \quad .$$

4.6.3 Calculation of iterations

Then the expression for G will be the following

$$G_1 = f_{\zeta\ *}\int_{-\infty}^{\infty}\eta_{tot}(w)\exp(\lambda w)\exp(-A\exp(\lambda w))dw\frac{6\exp(cz)}{c^4} \quad ,$$

where

$$A = f_{\zeta\ *} n_\infty \frac{\exp(-ca)}{c} \quad .$$

When $\eta_{tot} = const$, the integral can be taken which leads to

$$G_1 = f_{\zeta\ *}\eta_{tot}\frac{1}{\lambda A}\frac{6\exp(cz)}{c^4} \quad .$$

Note that the integral can be taken in the final limits which allows to take into account only the finite region of activities.

When η_{tot} is approximated by the polynomial it is easy to note that each monom in the integral leads to some elementary functions with the universal constants which can be seen from the translation of the variable in $\int_{-\infty}^{\infty} w^m \exp(\lambda w)\exp(-A\exp(\lambda w))dw$ to the variable $\lambda w + \ln(A)$. Here the integration must be fulfilled in the infinite limits. The integrals are expressed through the values of the ψ-function and the derivatives when the argument is equal to 1.

The second approximation for θ gives the following result

$$\theta_2(z,w) = \exp(-f_\zeta\ {}_* n_\infty \exp(\lambda w) \int_{-\infty}^{z} \exp(cx - B\exp(cx))dx) \quad ,$$

where

$$B = \frac{\Gamma}{\Phi_*} f_\zeta\ {}_* \frac{6\eta_{tot}}{c^4} \frac{1}{\lambda A} \quad .$$

The integral can be also taken in the finite limits. After the integration we get

$$\theta_2(z,w) = \exp(-f_\zeta\ {}_* n_\infty \exp(\lambda w) \frac{1}{cB}(1 - \exp(-B\exp(cz)))) \quad .$$

For the final values one can get

$$\theta_2(\infty,w) = \exp(-f_\zeta\ {}_* n_\infty \exp(\lambda w) \frac{1}{cB}) \quad . \tag{4.6.28}$$

The value of B is obtained in the approximation $\eta = const$. For the further consideration the concrete values of B are not so important. It is important that in any possible case the functional dependence (also in the case $\eta_{tot}(w) = P_n(w)$) of G in the first approximation is the following

$$G_1 \sim const(z,w)\exp(cz) \quad .$$

Then B is some constant which allows the further calculation of the iterations.

The next step is the calculation of the total number of the droplets appeared in the considered period which can be done by the simple integration

$$N^{tot} = \int_{-\infty}^{\infty} dw N_{tot}(w) \quad .$$

Instead of

$$N^{tot} = \int_{-\infty}^{\infty} dw \eta_{tot}(w)(1 - \theta_2(\infty,w)) \quad ,$$

which can not be integrated we must take

$$N^{tot} = \int_{-\infty}^{\infty} dw \eta_{init}(w)(1 - \theta_2(\infty,w)) \quad ,$$

which gives the integral with no problem of convergence.

To calculate this integral we must note

$$\theta_2(-a,w) = \exp(-f_\zeta{}_* \exp(\lambda w) n_\infty \int_{-\infty}^{-a} \exp(cx - \frac{\Gamma}{\Phi_*} G) dx) \quad .$$

Consider now the case $\eta_{tot} = const$. After the evident renormalization of the variables of the integration the integral can be reduced to $\int_{-\infty}^{\infty} \exp(-\exp(x))(1-\exp(-H\exp(x)))dx$, where H is some constant. This value can be approximately calculated by the following procedure. Decompose the internal exponents and get

$$\begin{aligned} &\int_{-\infty}^{\infty} \exp(-\exp(x))(1-\exp(-H\exp(x)))dx = \\ &\int_{-\infty}^{\infty} \frac{1}{\sum_{i=0}^{\infty} \frac{\exp(ix)}{i!}} (1 - \frac{1}{\sum_{i=0}^{\infty} \frac{\exp(ix) H^i}{i!}}) dx = \\ &\int_0^{\infty} \frac{\sum_{i=0}^{\infty} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{\infty} \frac{y^i}{i!} \sum_{i=0}^{\infty} \frac{y^i H^i}{i!}} dy \quad . \end{aligned} \tag{4.6.29}$$

Note, that it is necessary to left the seria in the denominator.

The necessary accuracy will be ensured by the first three terms in the decompositions:

$$\int_0^{\infty} \frac{\sum_{i=0}^{\infty} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{\infty} \frac{y^i}{i!} \sum_{i=0}^{\infty} \frac{y^i H^i}{i!}} dy \quad .$$

Then an integral of the rational function can be simply calculated (also in the finite limits).

Calculate the integrals

$$I_j \equiv \int_0^{\infty} \ln^j y \frac{\sum_{i=0}^{\infty} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{\infty} \frac{y^i}{i!} \sum_{i=0}^{\infty} \frac{y^i H^i}{i!}} dy \approx \int_0^{\infty} \ln^j y \frac{\sum_{i=0}^{n-1} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{n} \frac{y^i}{i!} \sum_{i=0}^{n} \frac{y^i H^i}{i!}} dy \quad .$$

These integrals appear when the polynomial approximation for η_{tot}. is accepted.

Consider the function

$$f(y) = \ln^{i+1} y \frac{\sum_{i=0}^{n-1} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{n} \frac{y^i}{i!} \sum_{i=0}^{n} \frac{y^i H^i}{i!}} \quad .$$

as the function of the complex variable. Integrate this function along the closed path Ω, constructed in the following manner: the big circumference with the infinite radius; two straight lines $]y+i0,\infty+i0[$, $]y-i0,\infty-i0[$; the little circumference with the zero radius. The integrals along the circumferences are going to zero. The integrals along the straight lines give

$$\int [\ln^{j+1} y-(\ln y+2\pi i)^{j+1}\frac{\sum_{i=0}^{n-1}\frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{n}\frac{y^i}{i!}\sum_{i=0}^{n}\frac{y^i H^i}{i!}}dy \quad ,$$

which is reduced to I_j and $\sum_{k<j} e_k I_k$ with the known coefficients. On the other hand this integral is equal to

$$\sum res(\ln^{j+1} y\frac{\sum_{i=0}^{n-1}\frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{n}\frac{y^i}{i!}\sum_{i=0}^{n}\frac{y^i H^i}{i!}})$$

inside Ω. As the result we have the recurrent procedure which allows us to calculate all I_j.

Now let us see how the corrections due to the cut off can be introduced also in the value of $g(z,w)$. In the first approximation we have

$$g_1(z,w)=\frac{6f_*}{c^4}\exp(\lambda w)(\exp(cz)-\exp(-ca)) \quad .$$

The value of G_1 in the approximation $\eta_{tot}=const$ is given by

$$G_1=f_{\zeta\ *}\frac{\eta_{tot}}{6c^4}\frac{1}{A\lambda}(\exp(cz)-\exp(-ca)) \quad .$$

Note that it can be also calculated for the finite band of the activity spectrum. The calculations for the polynomial approximation for η_{tot} can be also fulfilled without difficulties.

Instead of the pre-exponential factor one can put some other function. The separation of this expression into the two factors - the first depended on λ and the second depended on z is obvious.

For θ_2 we get:

$$\theta_2(z,w)=\exp(-f_{\zeta\ *}n_\infty\exp(\lambda w)\int_{-\infty}^{z}\exp(cx-B(\exp(cx)-\exp(-ca)))dx)$$

and after the calculation:

$$\theta_2(z,w)=\exp(-f_{\zeta\ *}n_\infty\exp(\lambda w)$$

$$\exp(B\exp(-ca))\frac{1}{cB}(1-\exp(-B\exp(cz)))) \quad .$$

The final value is the following

$$\theta_2(z,\infty)=\exp(-f_\zeta\ {}_*n_\infty\exp(\lambda w)\exp(B\exp(-ca))\frac{1}{cB}) \quad .$$

It differs from (4.6.28) only by the renormalizing factor $\exp(B\exp(-ca))$.

The values of N^{tot} and $N^{tot}(z)$ are calculated in the same manner.

The estimates show that the second iteration gives the rather good approximation for the process of the nucleation. The reason is quite similar to the one dimensional case. Really, one can simply integrate all estimates from the one dimensional case to justify the validity of the obtained expressions.

One can see that all obtained values have the reduction of the expressions (or the arguments of the exponents) in two terms: one depended on λ and the other depended on z. This reduction can not be observed in the high iterations. It is responsible for the neglecting of the cross influence of the exhausting of the heterogeneous centers with the different activity. The similar property is absent in the situation of the decay. Here such cross influence can be neglected because when there are no sufficient number of the heterogeneous centers with the given activity immediately the moment of their exhausting will be earlier. In the situation of the decay all centers begin to take part in the process of the nucleation in one and the same time. Also it is necessary to stress that the equation on the parameters of the condensation balances the time of formation with the characteristic intensity of the formation. It leads to the fact that the characteristic width of the size spectrum in the dynamic conditions is always approximately equal to $\frac{1}{c}$.

The "active" part of the spectrum can have the very complicate form. It can initiate the essentially nonlinear character of the effective external conditions. From the above presented considerations it follows that the nonlinearity can have only the square character. The "approximate separation of activities" allows to fulfill the integration on the activities after the the solution of the separate problems on the level of the second iteration.

The structure of the construction of the solution under the nonlinear behavior of the external conditions in the modified method of the steepens descent prescribes to divide the region of the nucleation into the initial region and the region of the essential formation. The action of the initial supersaturation is included into the action of the droplets formed

in the initial region. Here one can see also the approximate separation of activities.

* * *

Recall that in the frames of the modified steepens descent method there occurs the natural extraction of the region of the appearence of the main consumers of the vapor. In this region the "ideal" behaviour of the supersaturation is known and one can easily establish the exhaustion of the heterogeneous centers. So, the necessary coefficients from this region can be calculated (even with some artificial[4] cross influence of the exhaustion of the heterogeneous centers). Later the behaviour of the supersaturation is known and one can calculate the evolution of the system by the explicit formulas. Again there is no cross influence (beside the artificial one) of the exhaustion of the heterogeneous centers. So, there appears the justification of the weakness of the role of the cross influence due to the exhaustion of the heterogeneous centers. The same reasons are the base for the approximate universality of the form of the spectrum as the function of the power of the exhaustion of the heterogeneous centers (see chapter 6).

4.6.4 Universal solution

Now the problem of construction of the universal solution will be considered. The idea of the universal solution lies in the fact that after the formation of the spectrum of the droplets the evolution depends only on the first three (and the zero) momentums of the distribution function. If one can choose some variables in which the solution (the distribution function) is the universal function (doesn't depend on the parameters of the problem) then the expressions for the momentums have the rather simple analytical structure which combines some parameters of the problem with the universal constants.

For the process of the pseudo homogeneous condensation the solution is obtained in the second chapter. For the heterogeneous condensation on the one sort of the heterogeneous centers the universal solution is absent, but the pseudo universal solution can be treated as the base for the further iterations.

Here the property of the universality can be observed in the case $\eta_{tot} = const$.

[4]In fact in frames of the given accuracy of the adopted procedure there is no cross influence of the exhaustion of the heterogeneous centers.

We shall rewrite the system of the condensation equations in the terms of ζ and Φ

$$\Phi_* + \frac{\Phi_*}{\Gamma} cz = \zeta + G \quad ,$$

$$G = \int dw g(w) \quad ,$$

$$g(w) = f_* \int_{-\infty}^{z} (z-x)^3 \exp(\frac{\Gamma}{\Phi_*}(\zeta - \Phi_*)) \theta(w,x) dx \exp(\lambda w) \quad ,$$

$$\theta(w) = \exp(-f_\zeta {}_* n_\infty \exp(\lambda w) \int_{-\infty}^{z} \exp(\frac{\Gamma}{\Phi_*}(\zeta - \Phi_*)) dx) \quad .$$

Introduce the function

$$\delta = \frac{\Gamma}{\Phi_*}(\zeta - \Phi_*) \quad .$$

Then after the substitutions

$$\lambda w \to w \quad ,$$

$$px \to x \quad ,$$

$$\frac{\Gamma}{\Phi_*} G \to G \quad ,$$

$$\frac{\Gamma}{\Phi_* \lambda} g \to g$$

one can get

$$\frac{c}{p} z = \delta + G \quad ,$$

$$G = \int dw g(w) \quad ,$$

$$g(w) = \frac{f_* \Gamma}{\lambda \Phi_* p^4} \int_{-\infty}^{z} (z-x)^3 \exp(\delta) \theta(w,x) dx \exp(w) \quad ,$$

$$\theta(w) = \exp(-f_\zeta {}_* \frac{n_\infty}{p} \exp(w) \int_{-\infty}^{z} \exp(\delta) dx) \quad .$$

Let us choose p as

$$\frac{f_* \Gamma}{\lambda \Phi_* p^4} = 1 \quad .$$

When the moment of t_* is chosen as the moment when the supersaturation attains maximum, then

$$\frac{c}{p} = \int dw 3 \int_{-\infty}^{z} (z-x)^2 \exp(\delta)\theta(w,x)dx \exp(w)$$

and there are no parameters in the expression for g. Then

$$f_{\zeta *}\frac{n_\infty}{p} = \frac{\Gamma^{1/4} f_*^{3/4} n_\infty}{\lambda^{1/4}\Phi_*^{1/4}} \quad .$$

The ordinary and natural condition to establish the zero point of activity can be written as the following one

$$\theta(w=0, z=\infty) = \frac{1}{2} \quad ,$$

which gives

$$f_* \frac{n_\infty}{\eta_{tot} p} = \frac{\ln 2}{\int_{-\infty}^{\infty} \exp(\delta(x))dx} \quad .$$

and there are no parameters in the last equation.

As the result there are no parameters in the system of equations and the solution has the universal form. All consequences now coincide with the analogous consideration from the second chapter.

The number of the droplets depends on f_* weakly. So we can get the equation on parameters in some rough approximation (see the iteration method) and then use the universal law.

4.6.5 Properties of the model

The results of the iteration procedure can give not only the description of the process of condensation but also the information about the form of the spectrum of activities. From the first point of view this question appears to be the external one respectively to the process of the droplets formation. The experimental results [32] show that the activity spectrums are rather smooth and have the form

$$\varphi(v) \sim v^{-(1+s)} \quad ,$$

where s is some small positive parameter. Here v has the sense of the activity introduced in a slightly another manner. The analysis of Smirnov

and Nadeikina shows that v is connected with the law of growth written in the following form

$$\frac{d\rho}{dt} \sim [\zeta - \frac{const}{\rho} + v\rho^{-3}] \quad .$$

From the last law the free energy can be reconstructed as

$$F = -\ln(\zeta + 1)\rho^3 + const\ \rho^2 + const\ v\ \ln\nu + const \quad ,$$

which leads to the approximate applicability of the linearization of $\Delta F = F_c - G = F(\rho_c) - F(\rho_e)$ as the function of w together with the identification of v as $w - w_0$ with some characteristic value of parameter w_0. Then η_{tot} can be presented as

$$\eta_{tot}(w) = \eta_{tot}(w_0)(w - w_0)^{-(1+s)} \quad . \tag{4.6.30}$$

The positive value of s ensures the convergence of the total number of the heterogeneous centers

$$\eta^{tot} = \int_w^\infty \eta_{tot}(w)dw \quad .$$

For the spectrums of such type (the long tail spectrum (LTS)) the region of the active heterogeneous centers is extremely important.

To present the most simple variant we shall assume that for f_{ζ_*} an approximation of the known form is adopted[5]

$$f_{\zeta_*} = f_{\zeta_{**}} \exp(\frac{\Gamma}{\zeta_{**}}(\zeta_* - \zeta_{**})) \tag{4.6.31}$$

with some constant value of the parameter Γ which leads to

$$\frac{\Gamma}{\zeta_{**}}(\zeta_* - \zeta_{**}) + \lambda w = -\ln[\frac{f_{\zeta_{**}} n_\infty}{c\ \ln 2}] \quad .$$

The last approximation is valid when the relative variation of ζ is small. In such a region we can put c in the r.h.s. of the last equation to some constant and get for the size spectrum

$$\mid f(z) \mid = \mid \eta_{tot}(w \mid_{w=\frac{const-cz}{\lambda}}) \mid \frac{c}{\lambda} \quad ,$$

[5]Index $**$ marks the basic points in this approximation.

where the dependence ln c is assumed to be unessential. Then one can see that in the case of (4.6.30) the convergence of the integral for G can be attained only if $s > 3$ (note that $c \to const \sim \frac{d\Phi}{dx}$ when $w \to \infty$). This result shows that LTS can not be effectively spread. This effect occurs only due to the approximation (4.6.31). Certainly, G is restricted by the value $\eta_{tot} z_{max}^3$, where z_{max} is the coordinate of the imaginary droplets formed when the supersaturation became slightly positive. In this situation the global behavior of the free energy at all values of the supersaturation appear. This doesn't allow to get any effective method for the condensation on the heterogeneous centers of the arbitrary nature.

Now the principle idea will be that some of heterogeneous centers had been exhausted in the previous processes of condensation occurred earlier. Then the balance equation will be the following

$$\frac{d\Phi}{dx} = c\frac{\Phi}{\Gamma} + 3\int_{-d}^{z}(z-x)^2 f(x)dx \quad ,$$

where d is some boundary parameter of the size spectrum initiated by the boundary of the activity spectrum. This equation can be solved. In the case of $\eta_{tot} \sim const$ we have

$$\frac{d\Phi}{dx} = c\frac{\zeta_{**}}{\Gamma} + 3\int_{-d}^{z}(z-x)^2 c(x)dx\frac{const}{\lambda} \quad . \tag{4.6.32}$$

Note that here $c\frac{\zeta_{**}}{\Gamma}$ is the derivative of the real (not the ideal) supersaturation on x. Having differentiated this equation three times we get the ordinary differential equation with the constant coefficients which has the well known solution.

Now the new principle of the self-consistency of the activity spectrum will be elaborated. We have noticed that the active centers have been exhausted in the previous processes of condensation. But the description of the previous processes of condensation is quite analogous to the description of the given process. As the result for the spectrum of the heterogeneous centers we have

$$\theta = \exp(-const\exp(\lambda w)\int_{-\infty}^{z}\exp(-\Gamma\frac{\zeta-\Phi_*}{\Phi_*})dx)$$

with the analytical structure

$$\theta(z \to \infty) = \exp(-const\exp(\lambda w)) \quad . \tag{4.6.33}$$

But this structure is already known - it is the structure of the final result and the start result for θ in the already investigated process. So, our start form was absolutely correct. Also it is very important that the structures of the expressions before and after the process coincide in the analytical form. This statement will be called as the principle of the self consistency of the activity spectrum.

Our initial conditions satisfies this principle. The process of the condensation conserves the analytical form of the activity spectrum and can be regarded as some shift in activities. Only some parameters are changed. We needn't to repeat the calculations as far as they are absolutely the same.

When $d \gg 1$, we needn't the details of the cut off of the spectrum and one can use the cut off by the Hevisaid function.

The last point of discussion is the possibility of the linearization of the external supersaturation. One can analytically prove the following statement.

- In the description of the condensation on the centers of the intermediate activity two manners of description covers all possible situations. These manners of description are:

  1). The supersaturation is absolutely determined by the consumption of the vapor by the droplets formed on the centers with the high activity[6].

  2) The linearization of the external supersaturation is possible during the period of formation of the droplets on the centers with the intermediate activity.

  The natural requirement for the activity spectrum is that the activity spectrum must be the smooth function with the cut off (or without the cut off) like (4.6.33).

The first manner of description is obviously trivial. The second is completely described here. Note that in the case when the spectrum has the pseudo singularities the last statement isn't valid and the special description is necessary.

[6]More precise:"which are essentially exhausted".

Chapter 5

Profiles of the condensation

All kinetic theories considered above use the free molecular character of the substance exchange between the vapor and the droplets. This implies the collective mechanism of the vapor consumption by the droplets. The vapor is considered in the system as the homogeneous one.

Due to the vapor consumption by the droplets there appeared the reduced density around every droplet. The density decreases when we approach to the droplet. The vapor consumption by the droplet is compensated by the diffusion.

In the many important situations the consumption of the vapor by the droplet can not be absolutely compensated by the diffusion. As the result some profile of the vapor appears. Only in the case of the *"pure free molecular regime of the substance exchange"* one can neglect this effect.

The analogous picture will appear in the distribution of the temperature around the droplet. The heat extraction leads to the increase of the temperature around the droplet. The mathematical structure in this case resembles the case of the density profiles. Here only the profiles of the density will be considered.

The situation of the decay will be taken as the example. The generalization for the dynamic conditions will be also presented.

All the results of the theory can be applied only in the cases when the critical embryo has at least a few dozens of the molecules, i.e. when the capillarity approximation can be applied. Such conditions will be

called as *the conditions of the capillarity approximation (CCA)* The inverse number of the molecules in the critical embryo will be the small parameter of the theory.

5.1 The profile of the separate droplet

Consider the process of the metastable phase decay.

The construction of the theory assumes some simplifications which are necessary to formulate the concrete mathematical model. These simplifications are based on some rigorous estimates which are presented below. The validity of CCA gives the restriction from above for the supersaturation in the system. Due to the vapor consumption by the droplets the supersaturation in the system can only decrease. This leads to the following

Statement 0.

If CCA is valid at the beginning of the process then CCA is valid during the whole period of the condensation.

Statement 1.

Under the CCA the main role in the vapor consumption is played by the super critical embryos, i.e. by the droplets.

The most simple way to prove it is to start from the free molecular regime and to prove this statement by the continuous transition to this situation. Also one can directly check this statement with the help of the final results.

The process of the condensation can be divided into some periods. At the initial period the rate of the nucleation is maximum. Later this rate decreases due to the consumption of the vapor by the droplets.

One can explicitly define the boundaries of PIFD.

The rate of the droplets growth is approximately proportional to the supersaturation of the vapor in the system. The rate of the formation of the new droplets is the very sharp function of the supersaturation. Under the essential violation of the rate of the droplets formation the rate of growth remains practically unperturbed.

Statement 2.

In the CCA the growth of the given droplet doesn't have any essential influence of the rate of growth of the neighbor droplets.

Then the evolution of the separate droplet can be the matter of the discussion.

The known expression for the stationary rate of nucleation assumes

that the density of the vapor is constant in time and the system is homogeneous in space. The following statement establish the connection between the stationary rate of the nucleation and the real rate of nucleation.

Statement 3.

In CCA during PIFD in the given spatial point in some moment of time the rate of nucleation approximately coincides in the leading exponential term with stationary rate of nucleation under the current characteristics of parameters.

This statement has at least two aspects - the variation of the density in time and the spatial variation of the density. To justify the last aspect one has to take into account the interpretation of the rate of nucleation as the probability to form the droplets in the given elementary volume. For the further considerations the main role played by the Bolzman equilibrium factor is important. This factor allows the clear interpretation as the probability. Only in the very small neighborhood of the droplets the conditions are essentially non stationary. These regions don't play any essentially role in the whole nucleation process.

Later it will be shown that the whole volume can be divided into two regions. In the first region ("unexhausted region" - UR) the density of the vapor is practically unperturbed and the rate of nucleation corresponds to the ideal rate of nucleation. In the second region ("exhausted region" - ER) the rate of nucleation is negligible in comparison with the rate of nucleation in the first region. Then according to the Statement 1:

In CCA the leading role in the process of the growth of ER belongs to the subregions around the super critical embryos (not around the small embryos).

Denote the concentration of the molecules in the vapor as $n(r)$. The evolution of the density profile in time t satisfies to the diffusion equation

$$\frac{\partial n}{\partial t} = D\Delta n \quad , \tag{5.1.1}$$

where D is the coefficient of diffusion. This coefficient is supposed to be approximately equal. The density n is now the function of the spatial argument r.

We shall present all construction for the diffusion regime of the substance exchange. As it will be seen later this regime is the worst one for some estimates to justify this approach.

As far as the density of the vapor is the function of the spatial coordinate the supersaturation of the vapor

$$\zeta = \frac{n(r) - n_\infty}{n_\infty} \tag{5.1.2}$$

is now also the function of the spatial coordinate. In the last expression the value of n_∞ is the concentration of the molecules in the vapor saturated over the plane surface of the liquid phase.

The value of the ideal supersaturation is introduced by

$$\Phi = \frac{n_{tot} - n_\infty}{n_\infty} \quad , \tag{5.1.3}$$

where n_{tot} is the total number of the substance in the unit volume[1]. This value isn't the function of the spatial point[2].

Consider the separate droplet. One can use the spherical symmetry and put the droplet in the center. The variable r will mark the distance from the center of the droplet. To solve (5.1.1), one can put the natural boundary conditions

$$n(r = \infty) = (\Phi + 1)n_\infty \quad , \tag{5.1.4}$$

$$n(r = r_k) = n^e \approx n_\infty \quad , \tag{5.1.5}$$

where r_k is the radius of the droplet and n^e is the concentration of the molecules in the vapor which is in the equilibrium with the embryo of the given size.

The stationary solution of the diffusion equation has a rather simple form[3]

$$n^s(r) = -\frac{\Phi n_\infty r_k}{r} + (\Phi + 1)n_\infty \quad . \tag{5.1.6}$$

On the base of the evident inequality

$$(\Phi + 1)n_\infty - n^s(r) \geq (\Phi + 1)n_\infty - n(r) \geq 0 \quad , \tag{5.1.7}$$

where $n(r)$ is the real concentration of the molecules in the vapor[4], it can be seen that the supersaturation $\zeta(r)$ can essentially deviate from Φ only

[1]The process of the diffusion is excluded from the consideration. The value of Φ is the imaginary supersaturation in the system where the formation of the droplets is forbidden. Then Φ is described only by the external conditions.

[2]In any case it isn't so sharp function as the real supersaturation is.

[3]One can also take into account the Steffan corrections.

[4]This inequality can be shown on the base of the superposition of the Green functions if one takes into account that the flow of the substance on the droplet grows in time.

when r is near r_k. The ratio $\exp(1)r/r(k)$ determines the characteristic scale of the region of the essential perturbation of the supersaturation (not the essential perturbation of the rate of nucleation).

When in the region $r \leq r_k \exp(1)$ one can see the stationary distribution of the density then the stationary flow of the molecules on the embryo can be introduced according to

$$j^s = -4\pi r^2 D \frac{\partial n}{\partial r} \quad . \tag{5.1.8}$$

The stationary approach to the calculation of the flow is valid in CCA. The distribution (5.1.6) of the density gives the following expression for the flow

$$j^s = -4\pi\Phi D r_k n_\infty \quad . \tag{5.1.9}$$

In the region $r \leq \exp(1)r_k$ due to the exponential approximation from the second chapter and $\Gamma \gg 1$ the rate of nucleation is negligibly small.

It is necessary to determine the profile of the density in the region $r \leq \exp(1)r_k$, to know j^s. Then the flow j^s is known on the base of (5.1.9). At the distances $r \gg r_k$ one can consider the droplet as the point source of the vapor consumption. Then the density of the vapor at $r \gg r_k$ can be obtained on the base of the Green functions method for the process of diffusion

$$G = \Theta(t) \frac{\exp(-\frac{r^2}{4Dt})}{(4\pi Dt)^{3/2}} \quad . \tag{5.1.10}$$

For the intensity of the vapor consumption by the point source situated[5] in the point $r = 0$ one can get

$$\frac{d\nu}{dt} = \lambda t^{1/2} \quad . \tag{5.1.11}$$

Here ν is the number of the molecules in the droplet and the constant λ is defined as

$$\lambda = (4\pi)^{3/2} (\frac{v_l}{2\pi})^{1/2} (\Phi n_\infty D)^{3/2} \quad , \tag{5.1.12}$$

[5]The analysis of the behavior of $n(r)$ on the base of superposition of the Green functions shows that in the region $r \leq r_k \exp(1)$ one can put $\Phi - \zeta_s \sim \Phi - \zeta$ where ζ_s is the supersaturation obtained on the base of the stationary approximation. So, one can use (5.1.11). As it will be seen later the most essential will be the asymptotes where $r \gg r_k \exp(1)$. To get these asymptotes one has to use the nonstationary approach because $\Phi - \zeta_s \gg \Phi - \zeta$ at these asymptotes. The approximation (5.1.11) can be interpreted as the initial approximation in the iteration procedure, the first step is given in this paper.

where v_l is the volume in the liquid for one molecule. For the total number of the molecules inside the droplet the following approximation is valid

$$\nu(t) = (4\pi)^{3/2}(\frac{3v_l}{4\pi})^{1/2}(\frac{2\Phi n_\infty D}{3})^{3/2}t^{3/2} \quad . \tag{5.1.13}$$

One can spread the rate of growth[6] of the droplets (5.1.13) for all values of ν and get

$$n(\infty) - n(r) = \int_0^t \frac{\lambda x^{1/2}}{8(D\pi(t-x))^{3/2}} \exp(-\frac{r^2}{4D(t-x)})dx \quad . \tag{5.1.14}$$

Having assumed[7] $n(\infty) = n_\infty(\Phi + 1)$, one can get

$$\Phi - \zeta(r) = c_0\Phi^{3/2}(\frac{v_l}{v_v})^{1/2}f(\beta) \quad , \tag{5.1.15}$$

where v_v is the volume in the saturated vapor for one molecule.

The precise derivation of the expression for the rate of nucleation can be given only under the free molecular regime of the substance exchange. According to the Statement 2 the characteristic size of the droplets during PIFD many times exceeds the critical size and there is no contradiction between the different regimes of the vapor consumption[8].

The exponential approximation accumulates the analytical structure and is based only on the estimate

$$I_s \sim \exp(-F_c) \quad .$$

This estimate is based on the Bolzman distribution which is valid. Only the value of F_c can be slightly reconsidered due to the diffusion regime of the evolution of the near critical embryos.

The function $f(\beta)$ has the form

$$f(\beta) = \int_\beta^\infty (\frac{1}{\beta^2} - \frac{1}{x^2})^{1/2} \exp(-x^2)dx \quad , \qquad c_0 = (\frac{2}{\pi})^{1/2} \tag{5.1.16}$$

[6]Use (5.1.11) for the super critical embryo. According to the Statement 2 we can consider only the super critical embryos and expand (5.1.11) until $\nu = 0$. This approximation leads to the relatively small errors. We must use for the stationary rate of nucleation the expression from the classical theory of nucleation which is obtained on the base of the precise law of the droplets growth.

[7]With the high relative accuracy.

[8]The diffusion regime can exist only under the gradient of the density in the presence of the flow. The critical embryo stays, thus, in the free molecular regime. Speaking about the critical embryo we imagine the small embryo which would grow in the free molecular regime.

and the variable β is defined according to

$$\beta = \frac{r}{2\sqrt{Dt}} \quad . \tag{5.1.17}$$

The universal profile is illustrated in the fig. 5.1.

At the arbitrary Knudsen numbers the value $\Phi - \zeta$ will decrease with the increase of r more rapid than in the considered case. This makes the strong inequalities from the base of this theory even more strong.

5.2 Approximation of the nucleation rate

The essential feature of (5.1.15) - (5.1.17) is the dependence of the profile of the supersaturation only on one variable β. Introduce the characteristic values β_{st} and β_{fin} by the following relations

$$f(\beta_{st}) = \frac{\Phi^{-1/2}(\frac{v_v}{v_l})^{1/2}}{\Gamma c_0 \exp(1)} \quad , \tag{5.2.18}$$

$$f(\beta_{fin}) = \frac{\Phi^{-1/2}(\frac{v_v}{v_l})^{1/2}}{\Gamma c_0} \equiv c_f \quad . \tag{5.2.19}$$

In the region of r corresponding to $\beta > \beta_{st}$, the rate of nucleation practically coincides with the unperturbed value $I_s(\Phi)$. It can be seen from the exponential approximation and from (5.1.15) - (5.1.17). For r corresponding to $\beta < \beta_{fin}$, the rate of nucleation is negligibly small. The values of r_{fin} and r_{st} are defined as the distances where β attains the values β_{fin} and β_{st}.

Consider the supersaturation in some spatial point r_0. For

$$t \leq t_{st} = \frac{r_0^2}{4\beta_{st}^2 D} \tag{5.2.20}$$

one can not observe any essential deviation of the rate of nucleation from the ideal value and for

$$t \geq t_{fin} = \frac{r_0^2}{4\beta_{fin}^2 D} \tag{5.2.21}$$

the rate of nucleation is negligible.

The equations (5.2.18), (5.2.19) lead due to $\Gamma \gg 1$ to

$$f(\beta_{st,fin}) \ll 1 \quad , \tag{5.2.22}$$

$$\beta_{st,fin} \gg 1 \quad . \tag{5.2.23}$$

For β, corresponding to the last inequality one can see the following asymptotic behavior

$$f(\beta) \sim \frac{\exp(-\beta^2)}{\beta^3} \quad . \tag{5.2.24}$$

It shows that the relative deviation of β_{fin} from β_{st} is rather small[9]. The value of the parameter

$$\delta = \frac{t_{fin} - t_{st}}{t_{fin} + t_{st}} \tag{5.2.25}$$

is also small.

The intensity (the probability) of the droplets formation in the relative time scale remains practically ideal and in one moment turns to be the negligible one. In the equations (5.2.18), (5.2.19) there is also the other parameter $(v_l/v_v)^{1/2}$. Then the validity (5.2.22), (5.2.23) isn't co evident. Practically in all situations δ is very small. We shall follow (5.2.22), (5.2.23), (5.2.24) and later the generalization will be given. The small value of δ together with the very smooth and weak unlinear behavior of $I_s(\zeta)/I_s(\Phi)$ as the function of ζ for $|\zeta - \Phi| \leq \Phi/2\Gamma$ allows to use the value of β_{eff} as some characteristic value defined by the following way. At the distances corresponding to $\beta > \beta_{eff}$ the rate of nucleation is the ideal one and at the distances corresponding to $\beta < \beta_{eff}$ the rate of nucleation is negligible.

Determine the variation in the total (over all volume) rate of the nucleation caused by the formation of the droplet of the given size. It is possible to introduce the parameter

$$k = \frac{\Gamma(\Phi - \zeta)}{f(\beta)\Phi} = \Gamma c_0 \Phi^{1/2} (\frac{v_l}{v_v})^{1/2} \quad . \tag{5.2.26}$$

The deviation from the maximal intensity is given by the following expression

$$\Delta I_s = I_s \int_0^\infty (1 - \exp(\frac{-\Gamma(\Phi - \zeta(r))}{\Phi})) 4\pi r^2 dr \quad , \tag{5.2.27}$$

[9] As it is seen in fig. 5.1. the values of β_{st}, β_{fin} are not so big. Then the asymptote (5.2.24) isn't so close to $f(\beta)$. But the final conclusion that the relative deviation of β_{st} from β_{fin} is small remains valid. Only this conclusion is important for the further consideration.

which can be reduced to

$$\Delta I_s = I_s 4\pi (2D^{1/2}t^{1/2})^3 \int_0^\infty (1 - \exp(-kf(\beta))\beta^2 d\beta \quad . \tag{5.2.28}$$

One can introduce the function ΔI^0 by the expression

$$\Delta I^0 = 4\pi (2D^{1/2}t^{1/2})^3 \int_0^\beta x^2 dx \quad . \tag{5.2.29}$$

The value of β_{eff} (and r_{eff}) is defined from

$$\Delta I^0(\beta_{eff}) = \Delta I_s \quad . \tag{5.2.30}$$

Inside the volume

$$V_{eff} = \frac{4}{3}\pi r_{eff}^3 \tag{5.2.31}$$

there is practically no nucleation. Outside this volume the rate of nucleation is practically unperturbed by the droplet situated at $r = 0$. The value of β_{eff} is constant during PIFD

$$\beta_{eff} = const = 3 \int_0^\infty [1 - \exp(-kf(\beta))]\beta^2 d\beta \tag{5.2.32}$$

and can be found from (5.2.30). The value of k as it can be seen from the r.h.s. of (5.2.26) isn't the function of r, β and t. On the base of β_{eff} one can get

$$r_{eff} = 2\beta_{eff} D^{1/2} t^{1/2} \quad , \tag{5.2.33}$$

which is the evident function of time. The volume V_{eff} grows in time as

$$V_{eff} = \frac{32}{3}\pi \beta_{eff}^3 D^{3/2} t^{3/2} \equiv c_v t^{3/2} \quad . \tag{5.2.34}$$

5.2.1 Kinetics of nucleation

Until this moment only the separate droplet was considered. This droplet was formed at $t = 0$. Now the interaction will be taken into account. The droplets can interact by the consumption of the vapor which leads to the variation of the rate of growth of the neighbor droplet. This interaction is rather weak according to the Statement 2. But one can take into account the interaction by the variation in the rate of nucleation. Note that

The relatively small variation of the supersaturation on the value Γ^{-1} *leads to the end of the nucleation.*

To have the opportunity to act on the rate of growth of the other droplet the given droplet have to be formed very close to the mentioned droplet. It can occur only at the moment of the formation of the given droplet and the probability is very low.

As far as we have seen that the essential deviation of the supersaturation from the ideal one can be seen in the region $r < r_k \exp(1)$ it means that the distance between the droplets must have the order less than $2r_k \exp(1)$. Then the time distance between the moments of the formation must by shorter than

$$\Delta t_{int} \sim [\frac{r_k}{\beta_{eff} D^{1/2}}]^2 \quad .$$

The duration of this period[10] is negligible in comparison with the characteristic duration of PIFD.

Every droplet forms rather rapidly the ER of such size which guarantees that the rate of growth of the given droplet can not be perturbed by the other droplets.

Three kinetic models will be considered in this section.

The model without the overlapping of the ER

The total volume W_{eff}, where the rate of nucleation is negligible can be approximately written in the following way

$$W_{eff} \sim \int_0^t c_v (t - t')^{3/2} P(t') dt' \quad , \tag{5.2.35}$$

where $P(t')$ is the probability of the droplets formation in the moment t'. For the values $P(t')$ one can approximately write the following equation

$$P(t') = I_s(\Phi)(1 - W_{eff}) \quad . \tag{5.2.36}$$

Two last equations form the closed system. Here the overlapping of the ER isn't taken into account.

[10]For $r \sim r_k$ one can not use the model of the Green functions. But as far as we need the estimate from above we can use instead of $r \sim r_k \exp(1)$ some other value of r corresponding to $r_k \ll r \ll N^{-1/3}$ where N is the total number of the droplets formed in the process of nucleation. For this value of r all considerations remain valid.

The system of the last two equations can be reduced to the Volterra equation. The kernel is rather trivial and it can be solved without any problems (after the Laplace transformation it is extremely simple).

The main disadvantage of this model is the absence of the overlapping of the ER initiated by the different droplets.

The model with the chaotic overlapping of the ER

Introduce the evolution equation for W_{free} which is the volume where the rate of nucleation coincides with the ideal value

$$-\frac{dW_{free}}{dt} = \frac{d\sum V_{eff}}{dt} W_{free} \quad , \tag{5.2.37}$$

where the sum is taken over all existing droplets. The term W_{free} in the r.h.s. of the last equation can be considered as the probability that the new ER is going to occupy the free (unoccupied) region. Taking into account

$$\frac{d\sum V_{eff}}{dt} = \sum \frac{dV_{eff}}{dt} \quad , \tag{5.2.38}$$

one can get

$$\frac{d\sum V_{eff}}{dt} = \frac{3}{2}\int_0^t c_v (t-t')^{1/2} P(t') dt' \quad , \tag{5.2.39}$$

where

$$P(t') = I_s(\Phi)(1 - W_{eff}) = I_s(\Phi) W_{free}(t') \quad . \tag{5.2.40}$$

Then it is possible to get

$$-\frac{dW_{free}}{dt} = \frac{3}{2}\int_0^t c_v (t-t')^{1/2} W_{free}(t') I_s(\Phi) dt' W_{free}(t) \quad . \tag{5.2.41}$$

After the integration of the last equation one can get

$$-\ln W_{free} = \int_0^t I_s(\Phi) c_v (t-t')^{3/2} W_{free}(t') dt' + const \quad . \tag{5.2.42}$$

Due to the initial conditions the constant *const* equals to zero. In terms of $F = -\ln W_{free}$ the last equation can be reduced to

$$F(t) = \int_0^t I_s(\Phi)(t-t')^{3/2} c_v \exp(-F(t')) dt' \quad . \tag{5.2.43}$$

The last equation has the mathematical structure considered in the second chapter.

In this model one can observe the chaotic overlapping of the ER. It can be seen in the first equation. One can analytically show that this approximation leads to some small influence on the PIFD and on the form of the spectrum of sizes.

The model with the formation of droplets inside the ER

Imagine that the ER appear also around the droplets formed in the ER of the other droplets. It is evident that this assumption isn't valid, but it allows to give some estimate and to clarify the sense of the first iteration in the method of disbalanced iterations.

The ER around the "new" droplets formed inside the ER of the "old" droplets can leave the ER of the "old" droplets. This leads to the error in the value of the volume where the nucleation is absent.

Instead of (5.2.40) in the frames of this model one has to use

$$P(t') = I_s(\Phi) \quad . \tag{5.2.44}$$

Then instead (5.2.41) one can get[11]

$$-\frac{\partial W_{free}}{\partial t} = \frac{3}{2}\int_0^t c_v(t-t')^{1/2} I_s(\Phi) dt' W_{free}(t) \tag{5.2.45}$$

and after the integration

$$-\ln W_{free} = \int_0^t I_s(\Phi) c_v (t-t')^{3/2} dt' + const \quad . \tag{5.2.46}$$

The value *const* equals to zero due to the initial conditions.

The role of this model can be seen from the last expression. This expression coincides in the functional form with the first iteration in the method of disbalanced iterations from the second chapter.

The results of the second and the third models are very close[12]. As the result one can see that the concrete account of the overlapping of the ER isn't important. This fact will be used later.

The alternative (and more clear) method can be reduced to the construction and justification of the psudomonodisperse approximations of

[11] Here there is the trace from the chaotic overlapping by the multiplication on W_{free}.

[12] See the method of the disbalanced iterations.

the previous chapter. It can be done on the base of the avalanche character of the disappearing of the UR. It can be proved on the base of the avalanche character of the growth of the ER around every separate droplet. This solves the problem of justification of the third and the second models.

5.2.2 Collective character of the vapor consumption

One has to generalize the theory for the arbitrary regime of the droplets growth. One can extract the following regimes.

- The pure diffusion regime of the droplets growth.

  This regime is extracted by the condition

  $$\frac{r_k}{R_{free}} \gg 1 \quad , \tag{5.2.47}$$

  where R_{free} is the mean length of the free motion of the molecule in the vapor and the coefficient of condensation α is canceled. This case was considered above.

- The arbitrary Knudsen numbers.

  This regime is extracted by the following condition

  $$\frac{r_k}{R_{free}} \sim 1 \quad . \tag{5.2.48}$$

  This situation can be described by the simple substitution of the intensity in (5.1.11) by the other intensity which can be obtained from the macroscopic law of growth which is known. The intensity of the droplets growth can be well approximated by the power dependence.

  Now consider the free molecular regime of the droplets growth. It is extracted by the condition

  $$\frac{r_k}{R_{free}} \ll 1 \quad . \tag{5.2.49}$$

  We can extract two subregimes

- The subregime of the pure free molecular growth.

  This regime is extracted by the following condition. The macroscopic law of the droplet growth is known. Then one can solve the stationary diffusion problem and get the profile. In the situation

$$\zeta(\infty) - \zeta(R_{free}) \ll \frac{\zeta(\infty)}{\Gamma(\zeta(\infty))}$$

  one can speak about the pure free molecular regime. This situation was considered in the second chapter.

- The regime of the intermediate free molecular growth.

  This regime was extracted by the same procedure but with the other condition

$$\zeta(\infty) - \zeta(R_{free}) \geq \frac{\zeta(\infty)}{\Gamma(\zeta(\infty))} \quad .$$

  The restriction (5.2.49) has to be observed. In this situation the evolution is rather complicate because it is necessary to take into account the existence of the profiles of the density and the elements of the collective consumption of the vapor.

  But the solution is rather simple. The equation (5.2.43) coincides in the mathematical structure with the balance equation in the second chapter. This fact shows that the second model describes this case also (with the renormalizations). In the second chapter one can note the following important fact

  The solution of the third model is the first iteration in the iteration solution of the second model (now we speak about the arbitrary regime of the droplets growth).

  The first iteration leads to the practically precise solution. The relative error calculated on the base of the first iteration is less than 0.02. It means that the solution of the second model practically coincides with the solution of the third model and with the help of the second model (with appropriate renormalizations) one can describe all situations. Certainly, the macroscopic laws of the droplets growth must be chosen in the appropriate manner.

  The similarity of the functional dependencies for the logarithm of the rate of nucleation in the situation of the vapor consumption and in the situation of the existence of the profile of the density

allows to reduce the problem of the description of the condensation to the choice of the superposition of the mentioned solutions. Then the problem is reduced to the algebraic problem and can be easily solved.

The analogous situation takes place with the inequalities (5.2.22), (5.2.23). Now it is clear that these inequalities aren't necessary. When they are not valid then the situation resembles the subregime of the intermediate free molecular regime. Then this situation can be solved in the analogous manner.

The approximate coincidence of the results of the second and of the third models has the important consequence. Extract the reason of such coincidence. The whole volume of the ER grows so rapidly that the droplets formed at the beginning (when the probability of overlapping of ER was very small) are the main consumers of the vapor. The ER around these droplets plays the main role in the ensemble of the ER around all droplets during PIFD. Then one can see that the problem of the overlapping isn't so important as it can be seen from the first point of view. This note is very important in the justification of the models. The approximation of the chaotic overlapping is rather precise because at the beginning the overleaping is small and when the overlapping is essential then the ER around the droplets formed in these moments don't play any essential role in the ensemble of the ER around all droplets formed during PIFD.

* * *

In the dynamic conditions the theory can be constructed by the formal generalization of the presented procedure.

In the first section the Statement 0 isn't valid. One has to require the CCA near the maximum of ζ. This requirement is natural because the majority of droplets is formed near the maximum of the supersaturation. This conclusion is based on the following *Statement 4*

For

$$\frac{d^2\Phi}{dt^2} \leq 0$$

it follows that

$$\frac{d^2\zeta}{dt^2} < 0$$

during PIFD

The possibility of the definition of the boundaries of PIFD is based on the last inequality together with the Statement 3

The function Φ introduced by (5.1.3) is now the function of time. One can analytically show the following statement.

The relative variation of Φ *during PIFd is small. The influence of the variation of* Φ *on* β_{st} *and on* β_{fin} *is negligible. The relative duration of PIFD is rather short.*

The last statement gives the base for the exponential approximation from the second chapter. According to the exponential approximation and the Statement 4 one can see that the relative variation of Φ has the order of Γ^{-1}

$$\frac{\Delta\Phi}{\Phi} \leq \Gamma^{-1} \quad . \tag{5.2.50}$$

According to the last statement[13] the function Φ as the function of time can be linearized practically in all situations

$$\Phi(t) = \Phi_* + ct \quad . \tag{5.2.51}$$

Here the index $*$ marks the value at some characteristic moment of time from PIFD, c is the parameter of the linearization.

According to the exponential approximation

$$I_s(\zeta) = I_s(\Phi_*) \exp(\frac{\Gamma}{\Phi_*} ct) \exp(\Gamma \frac{\zeta - \Phi_*}{\Phi_*}) \quad . \tag{5.2.52}$$

The value Φ_* is constant in time and in space.

According to (5.2.50) all equations connected with the consideration of the separate droplet remain valid. The r.h.s. of (5.2.18), (5.2.19) are now the functions of time but this dependence is the rather weak one. The perturbation of β_{st} and β_{fin} during PIFD is negligible. The results of the second section can be also applied.

In the description of the kinetics one has to put in the r.h.s. of (5.2.36) $I_s(\Phi)$ as

$$I_s(\Phi(t')) = I_s(\Phi_*) \exp(\frac{\Gamma}{\Phi_*} ct') \quad . \tag{5.2.53}$$

The same transformations can be also made in (5.2.40), (5.2.41), (5.2.42), (5.2.43), (5.2.44), (5.2.45), (5.2.46). The lower limit of the integration in (5.2.35), (5.2.39), (5.2.41), (5.2.42), (5.2.43), (5.2.45), (5.2.46) has to be chosen equal to $-\infty$. Then (5.2.43) becomes analogous to the balance equation from the second chapter. The last equation can be solved by

[13]This statement can be proved on the base of the iteration procedure.

iterations. The relation (5.2.46) corresponds to the first iteration. The relative error of the first iteration of the first model (which corresponds to the third model) is small. This error has to be calculated in the free molecular regime of the vapor consumption, where it is less than 0.15 (in the arbitrary regime it is less than 0.2).

The justification of the second and of the third model in the situation of the dynamic conditions can not be fulfilled by the same method as in the case of the decay of the metastable phase. The reason is the absence of the avalanche character of the back side of the size spectrum[14]. One has to formulate the alternative approach.

In the second model one can choose the scale of the variables x, z to put all coefficients except the intensity of the source to the unity. To attain maximum of the intensity at $z = 0$ it is necessary to take this coefficient A equal to 1.5 under the power 3 and 1.15 under the power 2 in the integral term[15]. The scales of the left halfwidth and of the write halfwidth are not so different. Then the droplets formed until $z_0 = -1/(2A)$ covers at $t(z_0)$ the rather small volume. The characteristic time of the droplets formation is $\Delta t = 1/A$. After $\Delta t + t(z_0)$ the intensity of the droplets formation is approximately equal to the intensity at $t(z_0)$. Then due to the sharp character of the intensity of the growth of the ER one can see that the volume of ER at $t(z_0)$ is relatively small.

Then one can assume with the good accuracy that the droplets formed until $t(z_0)$ covers the volume chaotically. The probability of the overlapping of ER around these droplets is very low and the probability that the place of the imaginary formation of the droplet is occupied by the ER is very small.

The justification of the chaotic character of the evolution until $t(z_0)$ allow to calculate the evolution of the ER from these droplets. One can determine the statistical characteristics and show that the model of the chaotic overlapping of these ER is rather precise.

We can not describe precisely the formation of the new droplets and the overlapping of the ER around these droplets. But the already known behavior of the ER around the droplets formed before $t(z_0)$ allows to give the estimate from above for the intensity of the formation. Having neglected the formation of the droplets after $t > t(z_0)$ one can get this estimate. This estimate is rather precise and is greater than the results

[14] But the avalanche character of the consumption of the vapor takes place.

[15] Consider two values of the power 2 and 3 in the integral term. It is convenient as far as the powers are the integer ones and practically covers all situations.

of the second model in the total number of the droplets[16] in 1.16 times for the power 2 and in 1.03 for the power 3. This dependence estimates the real evolution but not the second model from above.

At $t > t(z_0)$ as far as the integral term in the equation is now the integral with the separable kernel and the equation allows the analytical solution. The integral term transforms into the polynomial. One can see the good analytical approximation J_+ to the rate of nucleation. The constants in the polynomial behavior of $\ln J_+$ as the function of z can be determined by the unique numerical calculation. The main part of the spectrum is formed at $t > t(z_0)$. So, the analytical expression for the size spectrum is obtained. This procedure can be applied under the arbitrary behavior of the ideal supersaturation during PIFD. The analytical expression for the spectrum is now known.

Now it is necessary to get the estimate from below to the intensity of the droplets formation. The influence from the droplets formed at $t(z_0)$ is already described. Suppose that the droplets are formed at $t > t(z_0)$ with the intensity J_+. Also suppose that the ER around these droplets don't overlap. The whole ER is formed in the additive manner. The estimate from below is formulated. This procedure is the estimate from below also for the second model. It is rather precise and gives in the total number of the droplets the 0.837 of the result of the second iteration for the power 2 and 0.914 of the result of the second iteration for the power 3.

As the result the estimates from below and from above are formulated. The second model is justified. Then the third model is also justified. This procedure can be also applied in the situation of the decay.

The estimate from below at $t > t(z_0)$ is the analytical approximation. This approach can be used also for the collective regime of the vapor consumption. This approach can be used under the rather arbitrary behavior of the ideal supersaturation.

5.2.3 Comparison of the models

To compare the results with the already known approaches choose the situation of the decay.

Earlier the process of the condensation was described in [47], [33] with the help of the mean field theory. The profile of the density is supposed

[16]There is no justification of the second model.

to be the homogeneous one and the value of the density doesn't depend on the spatial point but only on time.

To clarify the difference between two theories introduce the "intermediate" theory. Suppose that instead of the real profile we have the profile corresponding to the density $n_\infty(\Phi+1-\frac{\Phi}{\Gamma})$ inside the ER and the density $n_\infty(\Phi+1)$ outside the ER. The boundary of the ER is chosen to ensure the necessary number of the molecules of the vapor initiated by the vapor consumption. The difference between two theories appears due to the effects of the overlapping and the nonlinear behavior of $\exp((\zeta-\Phi)\frac{\Gamma}{\Phi})$ as the function of ζ.

To construct the profile of the density in the intermediate theory it is necessary to spread the number of the consumed molecules with the relatively small difference between $n_\infty(\Phi+1)$ and $n_\infty(\Phi+1-\frac{\Phi}{\Gamma})$. This difference isn't directly determined by the rate of growth and doesn't depend for the separate droplet from the type of the theory. The size of ER many times exceeds the size of ER in the new theory (see fig. 5.2).

One can get in the diffusion regime the following expression for the ratio

$$\frac{(V_{eff})_{intermediate}}{(V_{eff})_{profile}} = \frac{\pi^{1/2}}{4}\frac{k}{\beta_{eff}^3}$$

with the parameter Γ and the relatively small values of the variable $(\frac{v_l}{v_v})^{1/2}$ in the parameter k.

The rate of the exhaustion of the free volume in the intermediate theory essentially exceeds this rate in the new theory. As the result the total number of the droplets many times exceeds the total number of the droplets in the theory of the mean field.

When the regime of the vapor consumption approaches to the free molecular regime the difference isn't so essential. The supersaturation falls at the distance R_{bound} (fig. 5.3) until the value which is relatively close to Φ and the nonlinearity in $\exp((\zeta-\Phi)\frac{\Gamma}{\Phi})$ doesn't lead to the order of the magnitudes. The absence of the units of $\frac{r}{2\sqrt{D}}$ shows the qualitative character of this illustration. The curves are drawn so close to the vertical axis in order to compare with fig. 5.2.

In the linear theory we can change the profile of the density by the arbitrary way. The results of the mean field theory approach to the results of the new theory. So, the inclusion of the given theory into the theory with the free molecular regime is observed.

* * *

The transition to the free molecular regime of the metastable phase consumption has some specific features. At some values of parameters there exists the situation when in the profile of the density of the given embryo there are several neighbor embryos also with the profiles of the density. The profile of the density cannot ensure the existence of the ER. The ER can appear only due to the superposition of the several profiles of the density. Earlier this situation was described by the superposition of the solutions in the limit situations of the collective consumption of the vapor and the individual formation of the profile. It was possible due to the similarity of the functional dependencies in the different models for the collective consumption and the individual formation of the profile.

In this situation one can speak about the collective formation of the profile of the density. One can consider this situation in the terms of ER only when the approximate additivity of the different profiles around the different droplets takes place. Earlier this opportunity was in the base of the first model where the ER can not cross. One has to investigate whether this approximate additivity remains valid in the kinetics of the process. One has to investigate this assumption only in the kinetics of the process.

Linearize the exponent corresponding to the exponent from the quantity of the condensated substance in the regime of the collective consumption. The regime of the substance exchange has to be taken as the free molecular one. Then one can get the following analog of the first iteration (the third model) having denoted via f_{add} the spectrum of the droplets sizes.

In the situation of the decay of the metastable phase

$$f_{add} \sim 1 - z^4 \quad ,$$

In the situation of the dynamic conditions

$$f_{add} \sim \exp(z)(1 - \exp(z)) \quad .$$

One has to show that these expressions are close to the results of the third model. In this case there appears the moment of the finish of the formation of the droplets. After this moment the spectrum becomes formally negative. One has to integrate until this moment and consider this moment as the final of PIFD.

The way to estimate the error in the total number of the droplets in this situation isn't so good. One can show this by the consideration of the dynamic conditions. It is necessary to put the maximums of the

additive spectrum and the spectrum of the third model to one point. Then

$$f_{add} \sim \exp(z + \ln(1/2))(1 - \exp(z + \ln(1/2))) \quad ,$$

$$f \sim \exp(z - \exp(z)) \quad .$$

Then it is necessary to reconstruct the write asymptote of the spectrum at the negative values of the argument. Then

$$f_{add} \sim 2\exp(z + \ln(1/2))(1 - \exp(z + \ln(1/2))) \quad ,$$

The integrals over these spectrums can be calculated explicitly and these integrals coincide. The number of the droplets coincide. But the spectrums don't coincide. It can be seen from the explicit picture (fig. 5.4).

On the fig. 5.4 one can see the first iteration and the additive analog which are normalized on the amplitude values. The conservation of the integrals over spectrums is attained by the renormalizations on the corresponding halfwidths. One can see that the difference is small but this difference exists. One has to take into account that the decomposition can be carried out from the middle point which decrease the error very essentially. These considerations are the very rough estimate from above. But even now one can see the negligible character of the errors of the approximation of additivity in the dynamic conditions.

In the situation of the decay the considerations are more simple. One needn't any shift or any renormalization because the initial moment is the moment of the amplitude value which is known. The spectrum in the first iteration as well as the spectrum in the additive model are drawn in fig. 5.5. One can see that they are rather close.

Now one can see the role of the first model which corresponds to the additive superposition of the ER. The extracted property of the approximate additivity of ER is important also for the justification of the possibility to neglect the fluctuations of the positions of the neighbor droplets of the form of the spectrum. In the intermediate situation the profile is the superposition of the few profiles. The concrete space distribution acts on the form of this profile. This space position fluctuates. Now the possibility to neglect the errors of the approximation of the additivity means the possibility to neglect the fluctuations of the distribution of the neighbor embryos.

Note that the approximation of the additivity has the sense only in the comparison with the other ("precise") models.

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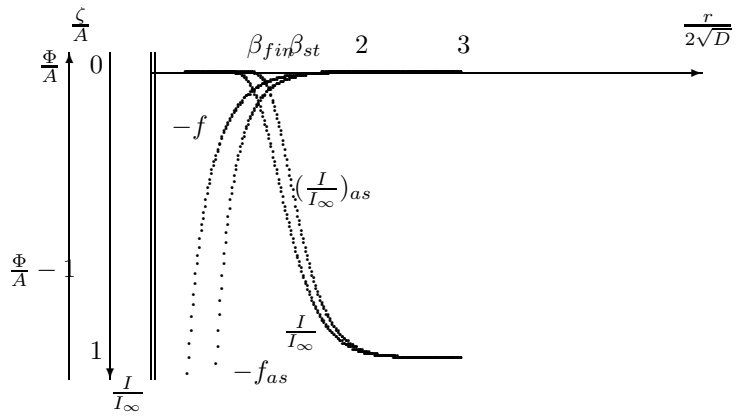

Fig. 5.1

Universal profile of the density $f(\beta)$, the relative intensity $\frac{I}{I(\infty)}$ and the asymptotes. Here $A = c_0\Phi^{3/2}(\frac{v_L}{v_v})^{1/2}$. In the calculation of the relative intensity $\frac{I}{I(\infty)}$ and the values β_{st}, β_{fin} the coefficient k was taken equal to 30.

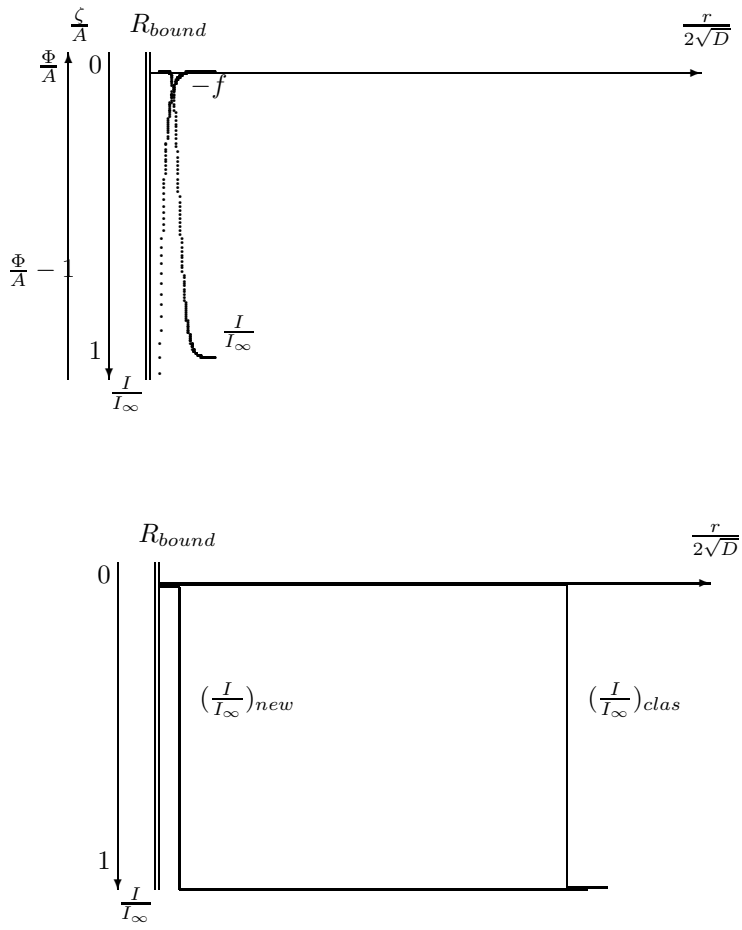

Fig. 5.2

The profile of the densuty, the relative intensity and the sizes of the ER arond the given droplet for the different models in the situation of some arbutrary Knudsen number. In the upper axis the function analogous to f, and the relative intensity $\frac{I}{I_\infty}$ are drawn. The value R_{bound} is determined as $max\{r_k, R_{free}\}$. In the lower axis the model profiles for the relative intensity in frames of the intermediate theory ("clas") and the theory with the profiles ("new") are drawn. The absence of the units of $\frac{r}{2\sqrt{D}}$ shows the qualitative character of this illustration.

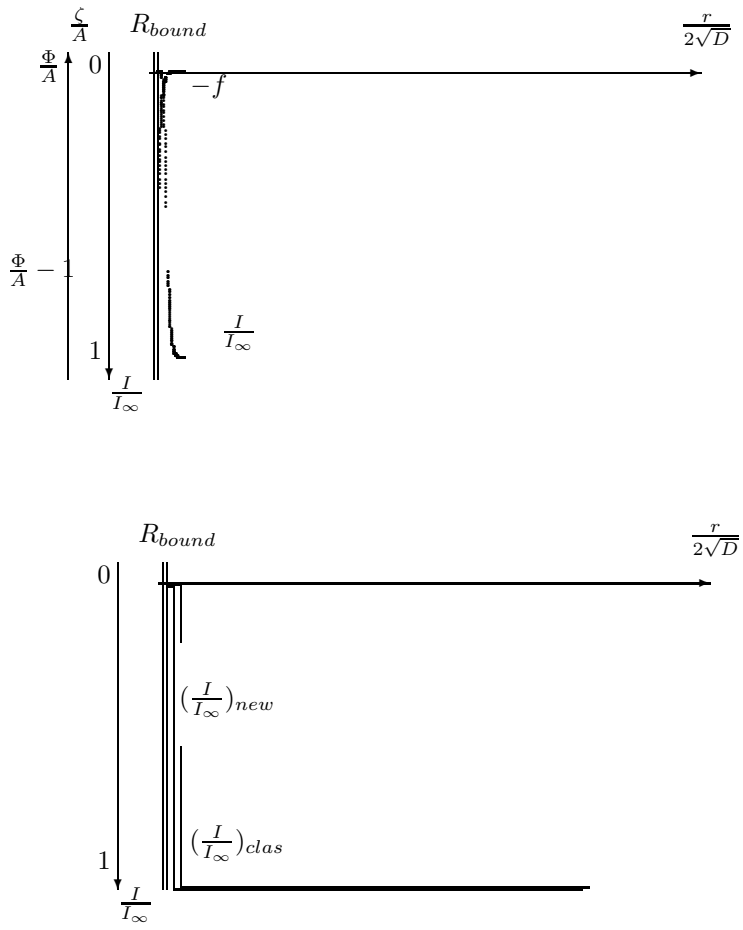

Fig. 5.3

The profile of the densuty, the relative intensity and the sizes of the ER arond the given droplet for the different models in the situation of the free molecular regime. In the upper axis the function analogous to f, and the relative intensity $\frac{I}{I_\infty}$ are drawn. The value R_{bound} is determined as $max\{r_k, R_{free}\} = R_{free}$. In the lower axis the model profiles for the relative intensity in frames of the intermediate theory ("clas") and the theory with the profiles ("new") are drawn. Here these values have one and the same order.

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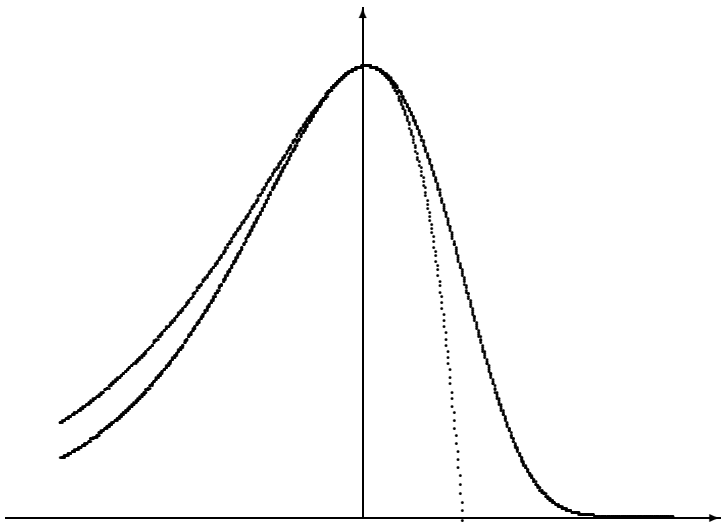

Fig. 5.4

Comparison of the spectrums in the dynamic conditions.

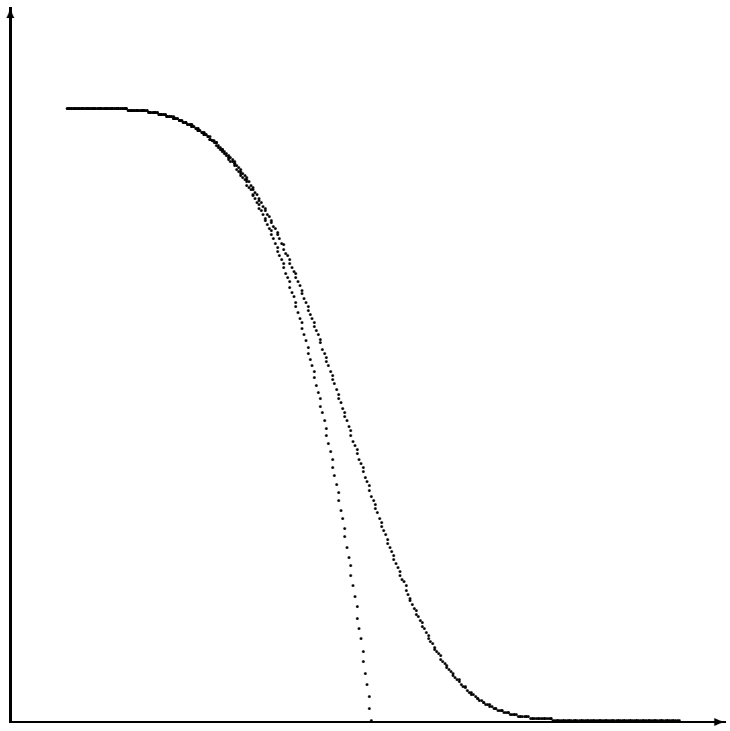

Fig. 5.5

Comparison of the spectrums in the situation of the decay of the metastable phase.

Chapter 6

Application of the universality

6.1 Thermal effects of the nucleation

One has to begin the inclusion of the temperature profiles by the determination of the stationary rate of nucleation. One can assume that in the near critical region there is the free molecular regime of the substance exchange. The rate of nucleation is determined in [57], [58] by the renormalizations

$$I_s = \frac{I_0}{1+k} \quad , \tag{6.1.1}$$

where I_0 is the stationary rate calculated without the thermal effects, k is defined according to

$$k = \frac{\beta^2}{c_v(1+p)} \quad , \tag{6.1.2}$$

β is the heat of the condensation of one molecule taken in units of k_bT, c_v is the heat capacity of the molecule of the substance under the constant volume, the parameter p is defined according to

$$p = (\frac{m}{m_g})^{1/2} \frac{n_g c_g}{n c_v} \quad , \tag{6.1.3}$$

n_g and n are the concentrations of the molecules of the passive gas and of the substance in the vapor, c_g is the heat capacity of the molecule of the passive gas, m_g and m are the masses of the molecules of the passive gas and of the condensated substance.

The concrete form of the renormalization isn't so essential. Only the smooth character of this renormalization as the function of the supersaturation is important. Then the approximation

$$I_s(\zeta) = I_s(\Phi)\exp(\Gamma\frac{\zeta-\Phi}{\Phi}) \tag{6.1.4}$$

remains valid. Parameter Γ remains the big parameter. Then the relative variation of the supersaturation ζ is rather small. Now it is initiated by the variation of the molecule number density n and the variation of the temperature T which leads to the variation of n_∞ according to the Klapeiron-Klausius equation

$$n_\infty(T) = n_\infty(T_0)\exp(\beta\frac{T-T_0}{T_0}). \tag{6.1.5}$$

The variations of n and n_∞ can not compensate each another in the expression for the supersaturation. So, these variations are also small when the variation of the supersaturation is small. It allows to present the following approximate form for the variation of the supersaturation

$$\Delta\zeta = \frac{-\mid\Delta n\mid}{n_\infty} - \frac{\Delta T}{n_\infty}\frac{\beta n}{T_0}, \tag{6.1.6}$$

where the variations are counted from some known values marked by the index "0". It is convenient to take the characteristics of the media as these values.

To get the renormalization (6.1.1) one has to use the "pure free molecular regime", i.e. $\Delta\zeta\mid_{R=R_{free}} < \frac{\zeta}{\Gamma}$. The decrease of ζ occurs due to the decrease of n and due to the decrease of T. The pure free molecular regime is absolutely natural for the small embryos[1].

One has to use together with the diffusion equation the following one

$$\frac{\partial T}{\partial t} = D_T\Delta T, \tag{6.1.7}$$

in the approximation of the continuous media where D_T is the coefficient of the thermal conductivity and Δ is the Laplace operator.

[1]The main difficulty is the non equilibrium character of the conditions for the critical embryo. The embryo has the temperature which differs from the temperature of the media. So the embryo isn't in the equilibrium with the media. One can only use the analytical expansions for the free energy of the embryo formation. This explains why only the weak thermal effects were considered in [58].

The structure and the solution of the equation of the heat conductivity are absolutely analogous to the diffusion equation. It allows to determine the phenomenological law of growth of the embryo. For the free molecular regime it is established in [53], under the intermediate Knudsen number it is determined in [34].

Only the dependence of $\frac{d\nu}{dt}$ on ν is interesting. One can observe the disappearing of the dependence on ν of the derivative of the free energy $\frac{dF}{d\nu}$ at the fixed temperature

$$\frac{\partial F}{\partial \nu} \to -\ln(\zeta + 1) \quad , \qquad \nu \to \infty. \tag{6.1.8}$$

The relative deviation of the temperature is determined from the equation of the heat balance

$$\frac{\beta}{k}\frac{\Delta T}{T_0} = 1 - \exp(\frac{dF}{d\nu} + \beta\frac{\Delta T}{T_0}). \tag{6.1.9}$$

The last value doesn't depend[2] on ν. The normalizing factor doesn't depend on ν and we have the previous functional dependence on ν. In any case this is connected with the phenomenological law of growth. It is supposed to be known.

All "Statements" formulated in the previous chapter remain valid.

The next step is the construction of the Green functions for the diffusion equation and for the heat conduction equation. When the rate of growth is known then the quantity of the extracted heat $\beta k_b T \nu$ is known. The intensity of the heat extraction is also known. Now the problems of the diffusion and of the heat conduction are the separate ones.

In the previous chapter the sharp front of the profile of the density has been established. It means that the intensity of the droplets formation around the given droplet can be approximately presented as the Hevisaid function of some shifted argument.

The functional form of the functional dependence is the same.

Due to (6.1.4) only the profile of the supersaturation is interesting. Due to (6.1.6) the profile of ζ can be approximately presented as the superposition of the profiles for n and for T. Then one can observe the superposition of the sharp fronts. The profile of the supersaturation has the sharp front also. This profile has the type of the Hevisaid function.

[2]To come to the first equation one has to cancel the kinetic coefficients in the balance equation. It can be done only when the regime of the substance exchange coincides with the regime of the heat exchange. But even when these regimes are different the appeared dependence will be weak.

The functional dependence on ν and on time is the same but the constants have to be changed.

The further consideration in the previous chapter was based on the sharp front of the profile of the intensity of the droplets formation. Here one can see the same property. The further consideration will be analogous to the previous chapter.

The continuous transition to the collective regime of the vapor consumption was based on the similarity of the profiles[3].

The role of the temperature T can be played by any other thermodynamic parameter. Certainly, one has to believe in the diffusion equation and in (6.1.4) with the big and approximately constant value of Γ.

6.2 Universal dependencies

Consider the dynamic conditions. The evolution equations can be written as

$$cz - \varphi(z) = A \int_{-\infty}^{z} K(z-x) \exp(\varphi(x)) dx \tag{6.2.10}$$

with some parameters c, A, the unknown function $\varphi(x)$ and the known kernel K. The function K is given by the macroscopic phenomenological law of the droplets growth. The relative growth of the function $K(z)$ is restricted by the values in two limit situations, i.e. by the relative growth of $K_{freemol}(z)$ under the free molecular regime and by the relative growth of $K_{diff}(z)$ under the diffusion regime of the growth

$$\frac{\frac{d}{dt} z^{3/2}}{z^{3/2}} \sim \frac{\frac{d}{dt} K_{diff}(z)}{K_{diff}(z)} \leq \frac{\frac{d}{dt} K(z)}{K(z)} \leq \frac{\frac{d}{dt} K_{freemol}(z)}{K_{freemol}(z)} \sim \frac{\frac{d}{dt} z^3}{z^3} \quad . \tag{6.2.11}$$

In the case of the power dependence of the law of growth

$$\frac{d\nu}{dt} \sim \nu^{\alpha} \tag{6.2.12}$$

the function K is given by the equation

$$K(z-x) \sim (z-x)^{\frac{1}{1-\alpha}} . \tag{6.2.13}$$

Then the evolution equation allows the renormalization and there remains only one parameter[4] c. Due to the choice of t_* as the moment of

[3] Even when the regimes and the powers don't coincide the required relation can be obtained on the base of the first iteration where there are no cross influence in the decrease of the supersaturation (the case is analogous to the condensation on the pseudo continuous set of the centers).

[4] The parameter A can be canceled by the renormalization of x.

the maximum of the supersaturation the value

$$c \sim \frac{1}{1-\alpha} \int_{-\infty}^{0} (z-x)^{\frac{1}{1-\alpha}-1} \exp(\varphi(x)) dx \qquad (6.2.14)$$

is the universal constant. Then the solution $\varphi(z)$ is also the universal function. The spectrum of sizes which is proportional to $\exp(-\varphi(x))$ is also the universal function. The form of the spectrum depends on α.

One can note the possibility of the more simple description of the process based on the first iteration in the iteration procedure

$$\varphi_{i+1}(z) = cz - A \int_{-\infty}^{z} K(z-x) \exp(\varphi_i(x)) dx, \qquad \varphi_0 = cz. \quad (6.2.15)$$

The spectrum of sizes f is described at some step of the iteration procedure as $f_i \sim \exp(\varphi_i(x))$ and the number of the droplets N_i is given by the integration of f_i from $-\infty$ till z.

The first iteration has the following form

$$\varphi_1(z) = cz - A \int_{-\infty}^{z} K(z-x) \exp(cx) dx. \qquad (6.2.16)$$

One can show that

$$\frac{d \mid N_i(\infty) - N_{i+1}(\infty) \mid / N_i(\infty)}{d\alpha} < 0. \qquad (6.2.17)$$

Analogous estimate can be given for the arbitrary Knudsen numbers

$$\frac{d \mid N_i(\infty) - N_{i+1}(\infty) \mid / N_i(\infty)}{d(R_k/R_{free})} > 0, \qquad (6.2.18)$$

where R_k is the radius of the droplet and R_{free} is the characteristic length of the free motion of the molecule in the vapor. After the notation that in the diffusion regime

$$\frac{\mid N_1(\infty) - N_2(\infty) \mid}{N_2(\infty)} \leq 0.25, \qquad (6.2.19)$$

one can show that the first iteration gives the good result for all regimes of the vapor consumption.

One has to analyze the first iteration. According to the properties of the exponent it can be calculated in any situation

$$\varphi_1 \sim cz - \exp(cz)\ const \quad const = A \int_{-\infty}^{0} K(y) \exp(cy) dy. \qquad (6.2.20)$$

The value of the constant has to be determined from the condition that t_* corresponds to amplitude value of the intensity of the droplet formation. Then

$$\frac{d\varphi_1}{dz} \mid_{z=0} = c - const\ c\ \exp(cz) \mid_{z=0} = 0 \tag{6.2.21}$$

and as the result

$$const = 1 \tag{6.2.22}$$

for all regimes of the vapor consumption. The universal form of the spectrum for all regimes of the vapor consumption

$$\varphi \sim \exp(x - \exp(x)) \tag{6.2.23}$$

is established. This distribution is taken in the units of the natural argument cx.

Here as in the procedure of the disbalanced iterations the choice of t_* is unique for all iterations and is the abstract[5]. The value of t_* is determined after the calculation of the last (precise) iteration. The power dependence for K isn't necessary.

The universal character of the obtained solution initiates the attempts to find the universal dependencies at the other periods of the process. One can consider the process of the coalescence [45].

The asymptote for the distribution function during the coalescence depends on the regime of the droplets growth. One can give the more approximate and more general formulation of the expression for the spectrum of sizes. Recall that the spectrum of sizes $P(u)$ is determined by

$$P(u) \sim \frac{\exp(\tau(u))}{-v_u},$$

where the function v_u is the velocity of the growth of the special size u on the special time variable τ and the function $\tau(u)$ is given by

$$\tau(u) = \int_0^u \frac{du}{v_u}.$$

To get the concrete dependencies it is necessary to know the function v_u. It supposed that for the big values of the size of the embryo the velocity of the growth of this value doesn't go to the constant.

[5]The value t_* and all values at t_* have to be considered as some external parameters. Contrary to [42] the uniqueness of the choice allows to cancel the parameters and get some universal dependencies.

The construction of the Lifshiz-Slezov asymptote is based on the following analysis. The unique possible opportunity of the behavior of the supersaturation must ensure the negative velocity of the relative number of the molecules in the embryo (with respect of the number of the molecules inside the critical embryo) except one point $u = u_0$ where the curve of this functional dependence attains zero.

The neighbor of this point corresponds to the singularity of $P(u)$ (this singularity is compensated by the zero in the denominator) and makes the main contribution in the subintegral function $\tau(u)$.

The point u_0 is the local maximum of the mentioned velocity as the function of size. In the neighborhood of the maximum it is natural to approximate by the square dependence

$$v_u = -\alpha(u - u_0)^2.$$

This approximation leads to

$$\tau(u) = const \ - \frac{1}{\alpha} \frac{1}{u - u_0}.$$

Having introduced the variable

$$z = \alpha(u - u_0),$$

one can get for the distribution $P(z)$ on z

$$P(z) \sim \frac{\exp(-1/z)}{z^2}.$$

The normalizing constant can be determined by the integration.

This distribution is the universal one. It is valid at the negative values of the argument. At the positive values of the argument it must be put to zero. One has to check all assumptions of the physical base of the theory of the coalescence.

6.3 Heterogeneous condensation

Obtain the evolution equations for the heterogeneous condensation in the dynamic conditions. The heterogeneous centers are distributed in the space homogeneously. But in the ER they are distributed unhomogeneously. At the center of every ER there is the center. All other centers

are distributed homogeneously[6]. Taking into account that the intensity is proportional to W_{free} and to the number of the free heterogeneous centers η one can formulate the evolution equations. It is necessary to add into all integral terms of the three models the value η and write for η the evolution equation

$$\eta(t) = \eta(-\infty)\exp(-const\int_{-\infty}^{t} I_s(\Phi_*)\exp(\frac{\Gamma}{\Phi_*}ct)(1-W_{eff})dt) \quad (6.3.24)$$

for the first model,

$$\eta(t) = \eta(-\infty)\exp(-const\int_{-\infty}^{t} I_s(\Phi_*)\exp(\frac{\Gamma}{\Phi_*}ct)W_{free}dt) \quad (6.3.25)$$

for the second model and

$$\eta(t) = \eta(-\infty)\exp(-const\int_{-\infty}^{t} I_s(\Phi_*)\exp(\frac{\Gamma}{\Phi_*}ct)dt) \quad (6.3.26)$$

for the third model. Here $\eta(-\infty)$ is the initial value for the quantity of the heterogeneous centers, W_{free} is defined analogously to the case of the density profiles.

These equations correspond to the exhausting of the heterogeneous centers with the fixed value of the total number in time.

The mentioned equations have to be closed by the following equations for the first model:

$$-W_{eff} \sim \int_{-\infty}^{t} (t-t')^{3/2} I_s(\Phi_*)\exp(\frac{\Gamma}{\Phi_*}ct')(1-W_{eff})\eta(t')dt'; \quad (6.3.27)$$

for the second model:

$$-\ln(W_{free}) \sim \int_{-\infty}^{t} (t-t')^{3/2} I_s(\Phi_*)\exp(\frac{\Gamma}{\Phi_*}ct')W_{free}(t')\eta(t')dt'; \quad (6.3.28)$$

for the third model:

$$-\ln(W_{free}) \sim \int_{-\infty}^{t} (t-t')^{3/2} I_s(\Phi_*)\exp(\frac{\Gamma}{\Phi_*}ct')\eta(t')dt'. \quad (6.3.29)$$

[6]One has to take into account the sharp character of the evolution analogous to those used in the justification of the three models. Or the centers will be distributed in a rather complicate way.

The generalization to the arbitrary Knudsen numbers is attained by the substitution of $(t-t')^{3/2}$ by some function $K(t-t')$ chosen from the phenomenological law of growth.

The inclusion of these models into the corresponding models obtained from the formal generalization of the regime of the droplets growth is rather ordinary. This procedure is quite analogous to the case of the homogeneous condensation but with one specific feature. The third model doesn't correspond to the first iteration, but corresponds to the precise solution of the system where for W_{free} the approximation of the first iteration is taken.

The iteration approximation in the solution of the second model with the two positive parameters $const_1$ and $const_2$ can be written in the following manner

$$\ln(W_{free\ i+1}) = const_1 \int_{-\infty}^{t} K(t-t') I_s(\Phi_*) \exp(\frac{\Gamma}{\Phi_*} ct') W_{free\ i}(t') \eta_i(t') dt', \tag{6.3.30}$$

$$\eta_{i+1}(t) = \eta(-\infty) \exp(-const_2 \int_{-\infty}^{t} I_s(\Phi_*) \exp(\frac{\Gamma}{\Phi_*} ct') W_{free\ i} dt'), \tag{6.3.31}$$

$$\eta_0 = \eta(-\infty), \qquad W_{free\ 0} \sim 1. \tag{6.3.32}$$

The analysis of this procedure shows the inclusion at $const_2 \to 0$ into the corresponding iteration scheme for the homogeneous condensation. One can show that

$$\frac{d \mid N_2(\infty) - N_3(\infty) \mid / N_3(\infty)}{d(const_2)} < 0, \tag{6.3.33}$$

which estimates the error of the iteration procedure by the homogeneous situation[7]. Already the first iteration leads to the rather precise result

$$-\ln W_{free\ \ 1} \sim const_1 \exp(\frac{\Gamma}{\Phi_*} ct) const_3, \tag{6.3.34}$$

$$const_3 = \int_{-\infty}^{0} K(-t') I_s(\Phi_*) \exp(\frac{\Gamma}{\Phi_*} ct') dt' \eta(-\infty), \tag{6.3.35}$$

[7]More precisely one has to note that the last inequality can be violated near the pseudo homogeneous limit, but only at the very small interval where this derivative is slightly positive. It allows to the possibility of the estimate of the error by the pseudo homogeneous situation.

$$\eta_1 = \eta(-\infty)\exp(-const_2 I_s(\Phi_*)\frac{\Phi_*}{\Gamma c}\exp(\frac{\Gamma}{\Phi_*}ct)). \tag{6.3.36}$$

Note that the variables z, x play the same role as t, t' play. The function K can be constructed in the following manner. Having integrated the law of growth $d\nu/dt$ one can find the dependencies $\nu(t)$ and $t(\nu)$. This dependence allows to extract the characteristic of the droplet y, which depends on ν and has the constant rate of growth (is proportional to time). The value of y for the droplets formed at $t = t_*$, will be marked by z and the value of x is determined as $y = z - x$. The dependence of ν on y gives the function K. All droplets with the coordinate x were formed at $t(x)$. The droplets formed at t_*, have the characteristic z at the moment t. Now the correspondence $t(z)$ is established and the coordinates z, x are the equivalent ones.

The spectrum of sizes $f(x)$ has in the first approximation of the iteration procedure the following form

$$f_1 = W_{free\ 1}\eta_1 I_s(\Phi_*)\exp(\frac{\Gamma}{\Phi_*}lx) \sim\sim I_s(\Phi_*)\eta(-\infty) \tag{6.3.37}$$
$$\exp(\frac{\Gamma}{\Phi_*}lx - const_4\exp(\frac{\Gamma}{\Phi_*}lx) - const_1 const_3\exp(\frac{\Gamma}{\Phi_*}lx)),$$

where

$$l = \frac{d\Phi}{dz}, \tag{6.3.38}$$

$$const_4 = const_2 I_s(\Phi_*)\frac{\Phi_*}{\Gamma c}. \tag{6.3.39}$$

Now one can not consider t_* as the moment when the supersaturation maximum is attained. When t_* is chosen as the moment when the half of the total number of the droplets is formed then the system contains some parameter.

When we use for f the more complicate expression

$$f_i = W_{free\ i-1}\eta_i I_s(\Phi_*)\exp(\frac{\Gamma}{\Phi_*}lx), \quad i = 2, \tag{6.3.40}$$

there are no problems in the calculation of the total number of the droplets. As far as one can get η_i analytically the value $\int f_{i+1}dx$ allows the analytical calculation

$$\int_{-\infty}^{t_0} W_{free\ i}(t)I_s(\Phi_*)\exp(\frac{\Gamma}{\Phi_*}ct)\exp[-const_2 I_s\int_{-\infty}^{t}\exp(\frac{\Gamma}{\Phi_*}ct')$$

$$W_{free\ i-1}(t')dt']dt \sim \frac{1}{const_2} \tag{6.3.41}$$
$$[1 - \exp[-const_2 \int_{-\infty}^{t_0} I_s(\Phi_*) \exp(\frac{\Gamma}{\Phi_*} ct') W_{free\ i}(t')dt']] \quad .$$

This corresponds to the balance of the heterogeneous centers. The integral of the spectrum can be calculated in the following form

$$\int_{-\infty}^{t_0} f(t)dt \sim \eta(-\infty) - \eta(t_0). \tag{6.3.42}$$

The concrete calculation of the iterations gives

$$W_{free\ 1} = \exp(-const_1 const_3 \exp(\frac{\Gamma}{\Phi_*} ct)). \tag{6.3.43}$$

In the second approximation the spectrum of sizes is given by

$$f_2(t) = W_{free\ 1} \eta_2 I_s(\Phi_*) \exp(\frac{\Gamma}{\Phi_*} ct), \tag{6.3.44}$$

and after the renormalization $\frac{\Gamma}{\Phi_*} ct \to t$

$$f_2 \sim I_s(\Phi_*) \exp(t) \exp(-const_1 const_3 \exp(t)) \eta(-\infty) \tag{6.3.45}$$
$$\exp[-\frac{const_2}{const_1 const_3} \frac{\Phi_* I_s(\Phi_*)}{\Gamma c} [1 - \exp(-const_1 const_3 \exp(t))]].$$

It can be reduced after the shift $y = t + \ln(const_1 const_3)$ to

$$f_2 \sim \frac{I_s(\Phi_*)}{const_1 const_3} \eta(-\infty) \exp(y) \exp(-\exp(y)) \exp[-\Delta[1 - \exp(\exp(y))]], \tag{6.3.46}$$

where

$$\Delta = \frac{const_2}{const_1 const_3} \frac{\Phi_* I_s(\Phi_*)}{\Gamma c}. \tag{6.3.47}$$

It seems that now it is possible to put the condition for t_* as the moment of the maximum intensity of the droplets formation (not the maximum of the supersaturation) and get the equation on Δ. The value Δ is now expressed through some constants which leads to the universal form of the spectrum f_2. One has to realize that the shift which is initiated by the transition to y doesn't allow the further shift which is

required by the choice of t_* as the moment of the maximal intensity of the droplets formation. One can not get the universal form of the spectrum. It can be also seen from the expression for the number of the droplets in the second iteration

$$N_{tot\ 2} \sim \int_{-\infty}^{\infty} f_2(t)dt \sim \eta(-\infty)[1-\exp[-const_2 I_s(\Phi_*)\frac{\Phi_*}{\Gamma c}\frac{1}{const_1 const_3}]], \tag{6.3.48}$$

which has the explicit dependence in a very complicate form.

The reason of the absence of the universality are the rather specific conditions of the problem. In the more general problem of the condensation on the spectrum of activities of the heterogeneous centers one can observe the universality.

One can describe the activity of the heterogeneous center by the parameter w from the expression for the probability of the formation on the given heterogeneous center

$$I_s = I_s(\Phi_*)\exp(w)\exp(\frac{\Gamma}{\Phi_*}ct)\eta(w,t). \tag{6.3.49}$$

The value of $\eta(w,-\infty)$ plays the role of the density of the distribution of the total number of the free heterogeneous centers. The differential evolution equation in the second model transforms in the diffusion regime into

$$-\frac{dW_{free}}{dt} \sim \frac{3}{2}\int dw I_s(\Phi_*)\exp(w)\int_{-\infty}^{t}(t-t')^{1/2} \tag{6.3.50}$$

$$W_{free}(t')\exp(\frac{\Gamma}{\Phi_*}ct')\eta(w,t')dt' W_{free}(t)$$

and the third model transforms into

$$-\frac{dW_{free}}{dt} \sim \frac{3}{2}\int dw I_s(\Phi_*)\exp(w) \tag{6.3.51}$$

$$\int_{-\infty}^{t}(t-t')^{1/2}\exp(\frac{\Gamma}{\Phi_*}ct')\eta(w,t')dt' W_{free}(t)$$

The integration of the known function together with the relation for η leads to the system of the equations

$$F = \int dw A\exp(w)\int_{-\infty}^{t}(t-t')^{3/2}\exp(t'-F)\theta_w dt \tag{6.3.52}$$

for the second model and

$$F = \int dw A \exp(w) \int_{-\infty}^{t} (t-t')^{3/2} \exp(t')\theta_w dt \tag{6.3.53}$$

for the third model and

$$\theta_w = \exp[-B\exp(w)\int_{-\infty}^{t} \exp(t'-F)dt'] \tag{6.3.54}$$

for both models with the coefficients[8]

$$B = I_s(\Phi_*)\frac{\Phi_*}{\Gamma c} \quad , \qquad A \sim (\frac{\Phi_*}{\Gamma c})^{5/2}\eta(-\infty)I_s(\Phi_*) \tag{6.3.55}$$

for the functions $F = -\ln W_{free}$ and $\theta_w = \frac{\eta(w,t)}{\eta(w,-\infty)}$ and for the variables w and $t \to t\frac{\Gamma}{\Phi_*}c$. Only the renormalization t without any shift has been done.

Define the zero points for t and w. As far as here there is the unlimited number of the heterogeneous centers one can use the moment of the maximum of the supersaturation as t_*. The zero point for w one can choose as the activity of the heterogeneous centers for which $\theta(w=0,\infty) = \frac{1}{2}$. It gives the following expressions for the constants A and B:

$$A = [\int dw \exp(w)\frac{3}{2}\int_{-\infty}^{0} (-t')^{1/2}\exp(t'-F(t'))\theta_w(t')dt']^{-1} \tag{6.3.56}$$

for the second model and

$$A = [\int dw \exp(w)\frac{3}{2}\int_{-\infty}^{0} (-t')^{1/2}\exp(t')\theta_w(t')dt']^{-1} \tag{6.3.57}$$

for the third model and

$$B = \ln 2[\int_{-\infty}^{0} \exp(t'-F(t'))dt']^{-1} \tag{6.3.58}$$

for both models.

The values A and B are the universal constants[9]. The solution is the universal function. The distribution of the droplets is also the universal function

$$f \sim \exp(t-F(t))\theta_w(t) \tag{6.3.59}$$

[8]The coefficient in the law of growth of ER is included in A.

[9]The values of A for the second and for the third models are very close.

of the variables t and w. This function depends on the regime of the droplets growth.

One can also see the natural inclusion of this situation which ensures the transition to the collective regime of the vapor consumption.

One has to stress the dimensionless character of the regularization which was used in the construction of the condensation on the continuous spectrum of the nucleus. One can use as the initial value the following function $\theta_{w\ 1}(t = -t_{00})$ ($t_{00} \sim 5$ isn't the parameter of the problem but only the parameter of the cut off). Then

$$\theta_{w\ 1}(-t_{00}) = \exp(-B\exp(w)\exp(-t_{00})). \tag{6.3.60}$$

After the substitution of the initial condition one can come to

$$F = \int dwA\exp(w)\exp(-B\exp(w)\exp(-t_{00})) \int_{-t_{00}}^{t}(t-t')^{3/2}\exp(t'-F(t'))\theta_w(t')dt' \tag{6.3.61}$$

for the second model and

$$F = \int dwA\exp(w)\exp(-B\exp(w)\exp(-t_{00})) \int_{-t_{00}}^{t}(t-t')^{3/2}\exp(t')\theta_w(t')dt' \tag{6.3.62}$$

for the third model and

$$\theta_w = \exp[-B\exp(w)\int_{-t_{00}}^{t}\exp(t'-F(t'))dt'] \tag{6.3.63}$$

for both models with the same parameters. Now θ_w has the sense

$$\theta_w = \eta(w,t)/\eta(w,-t_{00}). \tag{6.3.64}$$

For A and B one can come to some other expressions

$$B = \ln 2[\int_{-t_{00}}^{0}\exp(t'-F(t'))dt']^{-1} \tag{6.3.65}$$

for both models and

$$A = [\int dw \exp(w) \exp(-B \exp(w) \exp(-t_{00})) \\ \frac{3}{2} \int_{-t_{00}}^{0} (-t')^{3/2} \exp(t' - F(t`))\theta_w(t')dt']^{-1} \tag{6.3.66}$$

for the first model and

$$A = [\int dw \exp(w) \exp(-B \exp(w) \exp(-t_{00})) \\ \frac{3}{2} \int_{-t_{00}}^{0} (-t')^{3/2} \exp(t')\theta_w(t')dt']^{-1} \tag{6.3.67}$$

for the third model.

The value $t_{00} \approx 5$ appears after the renormalization and the shift on t to the moment of the maximal supersaturation.

All these dependencies are the precise ones[10].

These laws depend on the regime of the vapor growth. Now one can get the approximate form of the spectrum which is the universal for all regimes.

Under the intermediate Knudsen numbers it is necessary to substitute $(t - t')^{3/2}$ by the function $K(t - t')$. The velocity of the growth of K is supposed to be restricted from below by the diffusion regime and from above by the free molecular regime.

The system of the condensation equations has the from

$$F = \int dw A_0 \exp(w) \int_{-\infty}^{t} K(t - t') \exp(t' - F(t'))\theta_w(t')dt' \tag{6.3.68}$$

for the second model

$$F = \int dw A_0 \exp(w) \int_{-\infty}^{t} K(t - t') \exp(t')\theta_w(t')dt' \tag{6.3.69}$$

for the third model and

$$\theta_w = \exp[-B \exp(w) \int_{-\infty}^{t} \exp(t' - F(t')dt'] \tag{6.3.70}$$

[10]Under the natural assumption $\nu_c \to \infty$ (here ν_c is the number of the molecules inside the critical embryo). This limit ensures the validity of (6.1.4).

for both models where

$$A_0 = \frac{\Phi_*}{\Gamma c}\eta(-\infty)I_s(\Phi_*) \tag{6.3.71}$$

and the factor from the renormalization is included into K. The iteration procedure is defined for the second model according to

$$F_{i+1} = \int dw A_0 \exp(w) \int_{-\infty}^{t} K(t-t')\exp(t'-F_i(t'))\theta_{w\ i}(t')dt', \tag{6.3.72}$$

$$\theta_{w\ i+1} = \exp[-B\exp(w)\int_{-\infty}^{t}\exp(t'-F_i(t')dt'], \tag{6.3.73}$$

$$F_0 = 0 \quad , \qquad \theta_{w\ 1} = 1. \tag{6.3.74}$$

To calculate the iteration one has to introduce the regularization for the total number of the heterogeneous centers θ_{tot}

$$\theta_{w\ tot} = \exp[-const_4\exp(w)], \tag{6.3.75}$$

where

$$const_4 \sim B\exp(-t_{00}), \tag{6.3.76}$$

and to use (6.3.64). The calculations give

$$F_1 = const_5\exp(t), \tag{6.3.77}$$

$$const_5 = \int dw A_0 \exp[-const_4\exp(w)]\exp(w)\int_0^{\infty(t_{00})} K(\rho)\exp(-\rho)d\rho,$$

$$\theta_{w\ 2} = \exp[-B\exp(w)\frac{1}{const_5} \tag{6.3.78}$$

$$[\exp(-const_5\exp(-t_{00})) - \exp(-const_5\exp(t))]].$$

The constant $const_5$ contains the information about the regime of the droplets growth. But the concrete choice of the values $t = 0$ and $w = 0$ by the rules formulated above leads to

$$const_5 = 1 \quad , \quad B = \frac{\ln 2}{(\exp(-\exp(-t_{00})) - \exp(-1))}. \tag{6.3.79}$$

In the expression for the spectrum of sizes

$$f(w,t) \sim A_0 \exp(w) \exp(t - \exp(t)) \tag{6.3.80}$$
$$\exp[-B \exp(w) \int_{-\infty\ (-t_{00})}^{t} \exp(t' - \exp(t'))dt']$$

there are no parameters

$$\frac{f}{f(w=0,t=0)} \sim 2 \exp(1 + w + t - \exp(t)) \tag{6.3.81}$$
$$\exp[-\frac{\ln 2}{q - \exp(-1)} \exp(w)(q - \exp(-\exp(t)))] \quad .$$

Here $q = 1$, or $q = \exp(-\exp(-t_{00}))$.

The estimate of the error can be obtained analogously to the already investigated cases. The reason is that the cross influence of the exhaustion of the heterogeneous centers is the very fine effect and can not be observed in the second iteration. The error in the second iteration is less than 0.2. So, one can observe the universality also in the heterogeneous condensation.

The idea of the universal solution can be also applied to the kinetics of the decay. The central idea is the approximation of the spectrum by the rectangular. The rectangular form of the spectrum corresponds formally to the situation when the power in the integral term initiated by the regime of the droplets growth goes to the infinity[11]. On the level of the volumes it corresponds to the instantaneous transition for W_{free} from 1 to 0. One can analytically prove this approximation.

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6.4 Universality of spectrums in condensation on centers with different activity

As the result of the previous consideration one can analyze the situation in the collective regime of the vapor consumption and then fulfill

[11] In the dynamic conditions the universal solution is the first iteration which also corresponds to the infinite value of the power in the regime of growth.

some formal procedures described above. Now the matter of investigation will be the condensation under the collective regime of the vapor consumption.

6.4.1 Decay on the several types of the heterogeneous centers

The possibility of the general description in the situation of the decay is connected with the sharp back front of the spectrum.

In the situation with the spectrum of activities one can not at first solve the problem in the pseudo homogeneous situation. Then on the base of this known behavior of the supersaturation the number of the free heterogeneous centers and the number of droplets can not be obtained with the high accuracy. One has to formulate the ansatz for the rate of nucleation as the function of time. Then one has to determine the parameters of this ansatz. Then one can use the balance laws for the heterogeneous centers and get the result for the number of the heterogeneous centers and for the droplets. For simplicity we shall call the basic ansatz for the behavior of the supersaturation also as the spectrum.

Really the functions

$$\psi_i = \exp(-x^i)$$

at $i = 3, 4$ have the sharp back side. The spectrum can be approximated by the rectangular. One can analytically show that the spectrum is restricted by these two curves. The case $i = 3$ corresponds to the instantaneous exhaustion of the heterogeneous centers and the evolution is determined by the monodisperse spectrum. The case $i = 4$ corresponds to the first iteration in the pseudo homogeneous situation. The rectangular approximation for both of these cases establishes the rectangular ansatz.

The form of the spectrum in the "monodisperse approximation" is shown in fig. 6.1. The approximate coincidence of the spectrum in the monodisperse situation f_{appr} and of the first iteration for the pseudo homogeneous situation f_1 shows the applicability of this approximation. The first iteration has more sharp back side.

Such a simple form of the spectrum allows to investigate also the situation with the source of the heterogeneous centers. The "monodisperse" ansatz ψ_3 or the pseudo homogeneous ansatz ψ_4 give the form of the spectrum with a rather high accuracy. It is only necessary that the total number of the heterogeneous centers doesn't grow more rapid than t (or z). The intensity of the recombination of the heterogeneous

centers can be rather arbitrary[12]. Then one can apply the monodisperse ansatz (may be from the shifted argument). The further considerations are absolutely analogous.

6.4.2 Decay on the pseudo continuous set of the heterogeneous centers

The universal form of the spectrum allows to generalize the conditions of the problem. In this case there are no principal difficulties in comparison with the decay on the several types of the heterogeneous centers. One can analytically show that the form of the spectrum lies between ψ_3 and ψ_4. This solves the problem and reduces it to the set of the algebraic equations.

In the situation of the "developed spectrum of activities" the form of the spectrum coincides with the result of the monodisperse approximation.

One can investigate the regularization of the initial conditions. It is profitable to shift the point $w = 0$ to the activity where

$$\theta \mid_{w=0} (\infty) = \frac{1}{2}.$$

After the shift on w one can get

$$g = a_0 \exp(w) \int_0^z (z-x)^3 \exp(-G)\theta dx, \tag{6.4.1}$$

$$G = \int_{-\infty}^{w_+} g(w)dw, \tag{6.4.2}$$

$$\theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G)dx), \tag{6.4.3}$$

where w_+ is the artificial upper boundary of the spectrum of activities, $a_0,\ a_1$ are some constants. After the renormalization on z, x one can put $a_0 = 1$. The condition for $w = 0$ gives for a_1:

$$a_1 = \frac{\ln 2}{\int_0^\infty \exp(-G)dx}. \tag{6.4.4}$$

Then there is only one parameter w_+.

[12]The equilibrium value of the heterogeneous centers can increase but the second derivative on time (or on z) must be negative.

One can use in the explicit form for the natural initial conditions for the number of the heterogeneous centers. As the result of the process of the decay

$$\eta = \eta_{tot} \exp(-const\ \exp(w) \int_0^\infty \exp(-G)dx) \tag{6.4.5}$$

or

$$\eta = \eta_{tot} \exp(-const\ \exp(w) \int_{-\infty}^\infty \exp(x-G)dx) \tag{6.4.6}$$

after the condensation in the dynamic conditions where η_{tot} is approximately the constant value. Now the condition η_* has to be substituted by η_{tot}. In any case the integrals give some constants and the functional form is the following

$$\eta = \eta_{tot} \exp(-const\ \exp(w)), \tag{6.4.7}$$

or

$$\theta_{init} = \exp(-const\ \exp(w)). \tag{6.4.8}$$

Now the value of the cut off of the spectrum of activities w_+ is not essential as far as $\theta_{init}(w_+) \to 0$. It leads to the more natural definition of $w_+ \to \infty$ of the spectrum of activities without some artificial parameter w_+.

Substitute this functional dependence into the system of the equations. After the integration over w one can come to

$$G \sim \int_0^z \frac{(z-x)^3 \exp(-G)}{a + \frac{\ln 2}{\int_0^\infty \exp(-G(x'))dx'} \int_0^z \exp(-G(x'))dx'} dx, \tag{6.4.9}$$

where the coefficient a comes from the new form of the spectrum of the activities.

One can cancel the coefficient

$$\frac{\ln 2}{\int_0^\infty \exp(-G(x'))dx'}.$$

As far as $\int_0^\infty \exp(-G(x'))dx'$ has the values close to 1 this action leads to the unsufficient shift of the activities.

Then

$$G \sim \int_0^z \frac{(z-x)^3 \exp(-G)}{a + \int_0^z \exp(-G(x'))dx'} dx. \tag{6.4.10}$$

We are going to show that the form of the spectrum depends on a rather weakly. In the case $a \to 0$ the last equation can be reduced to

$$G \sim \int_0^z \frac{(z-x)^3 \exp(-G)}{\int_0^z \exp(-G(x'))dx'} dx, \tag{6.4.11}$$

which resembles the homogeneous case with the increasing function

$$\int_0^z \exp(-G(x'))dx'$$

in the denominator.

When $a \to \infty$, one has the pure homogeneous case

$$G \sim \int_0^z (z-x)^3 \exp(-G)dx. \tag{6.4.12}$$

Then the spectrum $\exp(-G)$ has the rather simple qualitative behavior

$$\exp(-G) \sim 1 \quad z < z_{bound},$$
$$\exp(-G) \sim 0 \quad z > z_{bound},$$

where the parameter z_{bound} corresponds to $G(z_{bound}) = 1$.

The function $\int_0^z \exp(-G)dx$ is not so sharp function of z as the function $(z-x)^3$ is. The behavior of this function is the following

$$\int_0^z \exp(-G(x'))dx' \sim z \quad z < z_{bound},$$

$$\int_0^z \exp(-G(x'))dx' \sim const \quad z > z_{bound}.$$

The qualitative behavior of G will be the same but the characteristic width z_{bound} of the spectrum will be the other.

To get the width of the spectrum rescale z to get $a+c$ in front of the external integral.

Then

$$G \sim \int_0^z \frac{(z-x)^3 \exp(-G)}{\frac{a}{a+c} + \frac{1}{a+c}\int_0^z \exp(-G(x'))dx'} dx. \tag{6.4.13}$$

The asymptotes will be the following

$$G \sim \int_0^z \frac{(z-x)^3 \exp(-G)}{1+0} dx, \tag{6.4.14}$$

when $a \to \infty$, and

$$G \sim \int_0^z \frac{(z-x)^3 \exp(-G)}{\frac{1}{c}\int_0^z \exp(-G(x'))dx'} dx, \tag{6.4.15}$$

when $a = 0$.

The value $c = 0.08$ is determined in order to have the coincidence of the length of the spectrum. The quantitative analysis shows that the forms of the spectrums $f \sim \exp(-G)$ will be approximately equal for all values of the parameter a. The numerical results in the upper part of the fig. 6.2. confirm this statement. We see that the curves $f_{(a=0)}$ and $f_{(a=\infty)}$ practically coincide.

The integral in the denominator can act on the process by the other way. It can attain some value and destroy the renormalization of the spectrum to give the standard length. The maximum of such influence is attained at $a \sim c$. This case is also drawn and one can see that the plain part of the spectrum has the same length as the plain part of the spectrum in the situation $a = \infty$ has. The slope in this situation is the same as in the case $a = 0$. As it follows from the fig. 6.2 this doesn't lead to the essential deviation of the form of the spectrum.

In the lower part of the fig. 6.2. the boundaries of the spectrum from below f_{bel} and from above f_{ab} are drawn for $c = 0.08$ and for arbitrary values of a. The form of the spectrum is the approximately universal function.

Now one can investigate the situation with the finite w_+. The analogous transformations lead to

$$G \sim \int_0^z (z-x)^3 \exp(-G) \tag{6.4.16}$$
$$\frac{[1 - \exp(-(a + const \int_0^x \exp(-G(x'))dx') \exp(w_+)]}{\frac{a}{a+c} + \frac{1}{a+c}\int_0^z \exp(-G(x'))dx'} dx \quad .$$

For $w_+ = -\infty$ we have the homogeneous situation. For $w_+ = \infty$ we have the already considered situation which lies not so far from the homogeneous case. Here the form of the spectrum is also close to the universal one. The physical reason of the universality is the sharp dependence $(z-x)^3$. The considerations of the previous section can be used here also. This leads to the same conclusions.

The approximate rectangular form of the spectrum is valid also in the situation with the source of the heterogeneous centers under the restrictions mentioned above.

6.4.3 Condensation in dynamic conditions on heterogeneous centers with pseudo continuous set of activities.

The case of the condensation on the several types of the heterogeneous centers can not lead to the additional effects in comparison with the chapter four.

Introduce the function

$$\delta = \frac{\Gamma}{\Phi_*}(\zeta - \Phi_*).$$

Then after the substitutions

$$\lambda w \to w,$$

$$px \to x,$$

$$\frac{\Gamma}{\Phi_*} G \to G,$$

$$\frac{\Gamma}{\Phi_* \lambda} g \to g$$

one can get

$$\frac{c}{p} z = \delta + G,$$

$$G = \int dw g(w),$$

$$g(w) = \frac{f_* \Gamma}{\lambda \Phi_* p^4} \int_{-\infty}^{z} (z-x)^3 \exp(\delta) \theta(w,x) dx \exp(w),$$

$$\theta(w) = \exp(-f_{\zeta *} \frac{n_\infty}{p} \exp(w) \int_{-\infty}^{z} \exp(\delta) dx).$$

Choose p as

$$\frac{f_* \Gamma}{\lambda \Phi_* p^4} = 1,$$

and then there are no parameters in the expression for g. If the moment t_* is chosen as the moment when the supersaturation attains maximum, then

$$\frac{c}{p} = \int dw 3 \int_{-\infty}^{z} (z-x)^2 \exp(\delta) \theta(w,x) dx \exp(w).$$

Then

$$f_{\zeta\ *}\frac{n_\infty}{p}=\frac{f_*^{3/4}n_\infty\lambda^{1/4}\Phi_*^{1/4}}{\eta_{tot}^{1/4}\Gamma^{1/4}}.$$

The ordinary condition for the zero point is the following

$$\theta(w=0,z=\infty)=\frac{1}{2},$$

which gives

$$f_*\frac{n_\infty}{p}=\frac{\ln 2}{\int_{-\infty}^{\infty}\exp(\delta(x))dx},$$

and in the last equation there are no parameters.

This can be shown also on the level of ER.

There is the property of the weak dependence of the total number of the droplets on f_*. Then one can get the equation on the parameters of the process in some rough approximation.

The last model has the evident disadvantage. The expression for G has no convergence. Really one can substitute the expression for g into the expression for G and fulfill the integration over w. Then

$$G=A_{00}\int_{-\infty}^{z}(z-x)^3\frac{\exp(\delta(x))}{\int_{-\infty}^{x}\exp(\delta(x'))dx'}dx,$$

where

$$A_{00}=\frac{f_*\Gamma}{\lambda\Phi_* p^3 n_\infty f_{\zeta\ *}}.$$

The evident necessary asymptote $G\to 0$, $z\to-\infty$ leads to $\delta(z)\to\frac{c}{p}z$, when $z\to-\infty$. Then the subintegral function has the asymptote $(z-x)^3$ which doesn't ensure the convergence. Then some regularizations are necessary. After the end of the process of the condensation the constant value of η transforms to

$$\eta_{new}=\eta_{old}\exp(-Q\exp(w)),$$

where Q is some constant, η_{old} is the old value of the heterogeneous centers, η_{new} is the new value of the heterogeneous centers.

We shall consider this value as the initial one and after the analogous transformations one can come to

$$G=\frac{f_*\Gamma}{\lambda\Phi_* p^4}\int_{-\infty}^{z}(z-x)^3\frac{\exp(\delta(x)}{Q+\frac{f_* n_\infty}{p}\int_{-\infty}^{z}\exp(\delta(x'))dx'}dx.$$

The coefficient $\frac{f_* n_\infty}{p}$ can be put to some constant (for example 1) after the choice of the scale of activities. This choice establish the corresponding choice of Q (it has the same dependence on the activity as $\frac{f_* n_\infty}{p}$ has). The limit $Q \to 0$ corresponds to the already considered situation. Now we have the more general equation which takes into account the power of the previous deformation of the activity spectrum. The solution depends on Q and isn't the universal. One can observe the inclusion of the distribution in the set of the distributions under the different powers of the deformations.

The case $Q = 0$ has to be described explicitly. We are going to show that the spectrum here also has the universal form.

When Q goes to zero the region where Q is unessential starts at z_l corresponding to

$$\int_{-\infty}^{z_l} \exp(\delta(x))dx \sim (p/c)\exp(cz_l/p) \approx Q,$$

and increases. The asymptote $(z-x)^3$ of the subintegral expression is attained from z_l until z which isn't connected with Q. Then the asymptotic region becomes greater and one can integrate only the asymptote and get $(z-z_l)^4/4$. Then one can come to the following expression for f_ζ:

$$f_\zeta \sim \exp(z - \alpha(z-z_l)^4),$$

where the scale z is chosen to get $c/p = 1$ and α is some constant. The value of α can be obtained from the requirement that $max\ f_\zeta$ is attained at $z = 0$. Then

$$\alpha = -z_l^{-3}/4.$$

The expression for f_ζ can be presented in the following form

$$f_\zeta \sim \exp(-\alpha z_l^4)\exp(-(z/\Delta)^2)\exp(-4\alpha z^3|z_l|)\exp(-\alpha z^4),$$

where Δ is the characteristic width

$$\Delta = (2|z_l|/3)^{1/2}.$$

At the characteristic scale $z \approx \Delta$ the arguments of the third and the fourth terms have the characteristic values $z_l^{-1/2}$ and z_l^{-1}. Then one can neglect these terms and the form of f_ζ is the following

$$f_\zeta \sim \exp(-(z/\Delta)^2)$$

and has no parameters after the rescaling[13] $z \to z/\Delta$. The universal form $\exp(\delta)$ ensures the universal expression for θ

$$\theta = \exp(-\exp(w)\frac{\ln 2}{\sqrt{\pi}}\int_{-\infty}^{z}\exp(-x^2)dx).$$

This universal form can be attained earlier than $Q = 0$ and has the evident sense.

The forms of the spectrum are drawn at fig. 6.3. The curves "a", "b", "c", "d" are the solutions of the following equation

$$z = A_1\int_{-\infty}^{z}(z-x)^3\frac{\exp(\delta(x))}{Q+\int_{-\infty}^{x}\exp(\delta(x'))dx'}dx$$

for the different values of Q ("a" : $Q = 10$; "b" : $Q = 1$; "c" : $Q = 0.001$; "d" : $Q = 0.0001$). The curve "a" practically coincides with "b", the curve "c" practically coincides with "d" for all x. The curve "e" is the gaussian spectrum $\exp(-x^2)$. The curve "f" is the universal form of the first iteration $\exp(x - \exp(x))$ after the renormalization and the shift.

For all possible values of Q the spectrum lies between the first iteration and the gaussian spectrum. The difference between the first iteration and the gaussian spectrum is rather small (less 0.2) and lies in the frames of the accuracy of the modern experiment[14]. The value A_1 has to be chosen to ensure the $max\ \delta = 0$ near the maximum of the supersaturation. For $Q \to 0$ the quantity of the substance in the droplets isn't small due to the known cubic asymptote and one has remove the choice of t_* from the previous conditions where $max\ \delta$ is attained at $z = 0$ to the new condition $max\ \delta = 0$. In the concrete calculations there is no need to satisfy this condition precisely because the form of the spectrum doesn't essentially depend under the choice of $max\ \delta$ near zero. It is shown at fig. 6.4.

The fig. 6.4. demonstrates the weak dependence of the form of the spectrum on the basic point for the linearization, i.e. on the choice of t_*. This property is important for the justification of the conception of the universal spectrum and can be shown analytically. This property is also important for the numerical calculations. For $Q = 10$ two values A_1 were chosen. This corresponds to the different ways of the choice of t_* or the choice of $max\ \delta$. Two curves for δ for different A_1 are drawn

[13]This rescaling cancel the artificial parameter z_l.

[14]This ensures the weak dependence in the choice of a. It is necessary for the self consistency of the theory.

at fig. 6.4a. The upper curve corresponds to $A_1 = 0.5$, the lower curve corresponds to $A_1 = 1$. At the fig. 6.4b the spectrums are drawn in the normalized coordinates. These spectrums practically coincide and one can see only the one curve.

The limit $Q \to 0$ is analogous to the condensation in the situation of the "wide spectrum". Here we have the additional difficulties. These difficulties appears from the asymptote $(z-x)^3$ for the subintegral function. Then the relative quantity of the substance in the droplets is greater than Γ^{-1}, the time of the formation of the spectrum is greater than $c^{-1}\tau/\zeta$, the quasi stationary approximation isn't valid. One has to reconsider the base for constructions.

The simplification goes from the asymptote $(z-x)^3$. This asymptote doesn't depend on the quasi stationary approximation. The big quantity of the substance in the droplets requires to reconsider the condition of the choice of t_*. The complicate form of the external supersaturation can lead to the new form instead of $(z-x)^3$ but the consideration is absolutely analogous.

The opposite situation corresponds to the standard iterations[15]. The final expression for θ and for the spectrum can be obtained (in the second approximation of the iteration procedure) on the base of the supersaturation calculated in the pseudo homogeneous situation. This analogy leads to the three important consequences. The "pseudo homogeneous" base for the final formulas has the certain universality. In the condensation on the one sort of the heterogeneous centers this universality can be violated by the variation of the vapor consumption. The result of the method of the disbalanced iterations is based on the first iteration which is more universal. The point $w = 0$ corresponds to $\theta_{final} = 1/2$. The value w can be reconstructed on the base of θ_{final} as

$$w = \ln(\frac{\ln \theta_{final}}{\ln(1/2)}).$$

The invariant $\ln \theta / \exp(w)$ can be obtained for the arbitrary z. The condensation occurs in the hierarchical manner[16]. Then one can consider the distribution $f(x, w)$ on two variables x and w as the formal generalization. This distribution is universal. The dependence on w is the

[15] Under the corresponding choice of the renormalization θ_{init} and the choice of the external supersaturation the iteration procedure can be applied in all cases with the "external" supersaturation.

[16] The shift and the zero point $w = 0$ depends on the parameters of the process and on η_{tot} also.

explicit one

$$f(x,w) \sim \exp(\delta(x)) \exp(-\exp(w))$$
$$\exp(\int_{-\infty}^{x} \exp(\delta(x'))dx' \frac{\ln 2}{\int_{-\infty}^{\infty} \exp(\delta(x'))dx'}) \exp(w).$$

The factor $\exp(\delta)$ is the universal base for this distribution. It is presented at fig. 6.3 and is called as the spectrum. The last equation is available for δ calculated on the base of the precise solution. For the approximation for δ one can take δ from the pseudo homogeneous situation determined by two ways. The first way is to take the first iteration. It doesn't depend on the regime of the vapor consumption. The second way is to take the precise pseudo homogeneous solution. It is more accurate but depends on the regime of the vapor consumption. It is also approximate as far as it is based on the pseudo homogeneous solution. But all these errors are rather small.

The second consequence is that now we know the ansatz to use the opportunity alternative to the regularization of θ. It contains the universal form of the spectrum and the approximate equation on the parameters in some rough approximation. One can use δ from the pseudo homogeneous situation or from the first iteration.

The third consequence appears in the frames of the method of the steepens descent. The form of the external supersaturation can be essentially non linear[17]. Then one has to use the steepens descent method. Due to negligible character of the cross effect of the exhaustion of the heterogeneous centers except the final formulas one can simply summarize all amplitudes of the distributions[18] over the activity, then get the result for the pseudo homogeneous situation and then apply the final expressions for the number of the heterogeneous centers on the base of the known supersaturation.

One can analytically show for $Q \geq 1$ that the difference in the forms of the spectrums between the precise solution and the pseudo homogeneous precise solution and between the precise solution and the first iteration decreases when Q increases. Also one can show that for $Q \geq 1$ the difference between the external supersaturation and the real supersaturation in some moment of time decreases[19] when Q increases.

[17] Under the specific form of η_{tot}. One can show that in any case the external case can be restricted by the linear and by the square terms at the period of the formation on the centers with the intermediate activity.

[18] The characteristic values of the distributions at t_*.

[19] Also at t_*.

Then the results of fig. 6.3 show that the required limit is attained already at $Q \geq 1$.

One can analytically show that the form of the spectrum lies between the gaussian spectrum and the first iteration (or between the gaussian spectrum and the pseudo homogeneous precise solution). From the fig. 6.3 it can be seen that the difference is small for all situations. This leads to the general approximate universality.

At the condensation on the separate sort of the heterogeneous centers the spectrum (taken as $\theta \exp(\delta)$) isn't the universal one. But this difference isn't so essential. One can analytically show that the form[20] of the spectrum transforms continuously from the case of the small number of the heterogeneous centers to the pseudo homogeneous case and lies between these two cases. When the relative number of the heterogeneous centers is small the first iteration $\exp(x - \exp(x))$ gives the precise expression. In the pseudo homogeneous situation the same first iteration is the base of the practically precise solution (this is the consequence of the effectiveness of the iteration procedure). The form of the spectrum varies rather unessential.

At the fig.6.6 the pseudo homogeneous situation and the first iteration are drawn. The lower curves correspond to the spectrums only after the preliminary renormalization. To put the maximums of the pseudo homogeneous solution and the first iteration $\exp(x-\exp(x))$ to the same point the coefficient has to be put 0.2. The first iteration is more curved than the precise solution. The further renormalization includes

- the rescaling of the height leading to the similar amplitudes of the spectrums
- the shift of the arguments leading to the same positions of the maximums,
- the rescaling of the argument leading to the similar integrals of the spectrums.

These renormalizations lead to the practically universal form of the spectrums.

The dependence of the pseudo homogeneous spectrum initiated by the behavior of the supersaturation is the universal one. This value approximately has the universal form as it follows from the fig. 6.5. One can see three curves there (from left to right on the both sides)

[20] After the rescaling.

- the curve for the weak exhaustion of the heterogeneous centers $(-ln(\eta(\infty)) \sim 0.001)$;
- the curve for the strong exhaustion of the heterogeneous centers $(-ln(\eta(\infty)) \sim 20)$;
- the limit case - the gaussian case

This universal form can be proved analytically.

All forms are between the first and the third curves.

All curves are drawn after the mentioned scaling transformations[21].

The approximate universal form can be seen here.

When the supersaturation is absolutely determined by the heterogeneous centers in the homogeneous condensation then the spectrum is close to the universal one. In all situations the spectrum monotonously transforms from the pseudo homogeneous condensation under the linear source to the gaussian spectrum. Then one can speak about the approximate universality in this case also.

6.5 The activation barrier of the small height

In the homogeneous condensation the small value of the activation barrier corresponds to the violation of the macroscopic description. But in the heterogeneous condensation the disappearing of the activation barrier corresponds to the approaching of the critical embryo to the equilibrium one. But both embryos can allow the macroscopic description. Here the investigation of the situation with the small activation barrier (but still the exponent of the activation barrier is the leading term in the expression for the rate of nucleation) is rather essential.

One has to get the functional dependence of the activation barrier height on the supersaturation. Introduce the value of the chemical potential in the embryo b_ν. It differs from the chemical potential b of the vapor (We speak about the excess of the chemical potential). Both chemical potentials are counted from the chemical potential of the saturated vapor.

The connection of F with the chemical potential is given by

$$\frac{\partial F}{\partial \nu} = b_\nu - b.$$

[21] The results of the other figures are also drawn after these transformations.

The free energy has the minimum and the maximum, b is constant. Then b_ν has one extremum and it is the maximum[22]. Suppose that the characteristic of the maximum is $\nu = \nu_0$ and the maximum is b_{max}.

Suppose (after Landau) that the chemical potential can be decomposed into the Tailor seria until the second term. Then

$$b_\nu = b_{max} - \frac{|b''_{max}|}{2}(\nu - \nu_0)^2.$$

For the critical and for the equilibrium embryo the chemical potential coincides with b. Then for ν_e and for ν_c one can get

$$\nu_c - \nu_0 = \nu_0 - \nu_e = [\frac{2}{b''_{max}}(b_{max} - b)]^{1/2}.$$

Introduce ϵ according to

$$b = b_{max}(1 - \epsilon).$$

Then

$$\frac{\partial F}{\partial \nu} = \epsilon b_{max} - \frac{|b''_{max}|}{2}(\nu - \nu_0)^2.$$

Having integrated the last equation over $\nu - \nu_0$ from

$$-\Psi = -\sqrt{2\epsilon b_{max}/|b''_{max}|}$$

to

$$\Psi = \sqrt{2\epsilon b_{max}/|b''_{max}|}$$

one can get for ΔF the following expression

$$\Delta F = \int_{-\Psi}^{\Psi} (\epsilon b_{max} - \frac{1}{2}|b''_{max}|(\nu - \nu_0)^2) d(\nu - \nu_0) = 4\frac{2^{1/2}\epsilon^{3/2} b_{max}^{3/2}}{3|b''_{max}|^{1/2}}.$$

The analogous functional dependencies were established in [37] for the macroscopic nucleus of the condensation. It was done there only for some concrete expressions for the chemical potentials in frames of the theory of the dilute solutions. Here the dependencies have the general form.

[22] We are speaking about the analytical continuation of these functions. It corresponds to the absence of the dependence of the ejection ability on the embryo. It is explained by the rapid relaxation of the characteristics of the embryo in comparison with the two elementary interactions with the vapor molecules.

Due to the known expression of the chemical potential of the ideal gas the variation of the chemical potential is approximately linear on the supersaturation at some small intervals

$$\delta b \approx \delta\zeta \frac{db}{d\zeta}.$$

The natural approximation for the rate J will be the following

$$J = J_{max} \exp(-\frac{42^{1/2}\epsilon^{3/2} b_{max}^{3/2}}{3|b''_{max}|^{1/2}}),$$

or

$$J = J_{max} \exp(-\frac{42^{1/2}(\zeta_{max} - \zeta)^{3/2}(\frac{db}{d\zeta})^{3/2}}{3|b''_{max}|^{1/2}}),$$

where the index max denote the values at $b = b_{max}$ and the analytical expansion for the rate of nucleation is taken.

The analogous relation is valid for the stationary distributions

$$f = f_{max} \exp(-\gamma(\zeta_{max} - \zeta)^{3/2}),$$

where

$$\gamma = \frac{42^{1/2}(\frac{db}{d\zeta})^{3/2}}{3|b''_{max}|^{1/2}}.$$

According to the previous results one can investigate the pseudo homogeneous situation.

In the moment $*$ from PIFD

$$b_* = b_{max}$$

will not be valid. The linear approximation on the supersaturation for the argument of the exponent in the last balance equation near b_{max} leads to the essential errors. Then there will be two basic (for expansions) values of the supersaturation: ζ_{max} and ζ_*. The balance equation can be obtained analogously and can be written under the free molecular regime in the following form

$$\Phi_* + const\ z = \zeta + \int_{-\infty}^{z} (z - x)^3 f_{max} \exp(-\gamma(\zeta_{max} - \zeta)^{3/2}) dx,$$

where Φ is the value of the ideal supersaturation which allows the linearization on time and on z, x.

Introduce

$$\Phi_{*max} = (\Phi_* - \Phi_{max})\gamma^{3/2}.$$

The characteristic moment is the moment of the maximum of the supersaturation. Then after the rescaling one can get

$$\Phi_{*max} + cz = \delta(z) + \int_{-\infty}^{z} (z-x)^3 \exp(\delta^{3/2})dx,$$

where

$$c = 3\int_{-\infty}^{0} (z-x)^2 \exp(\delta^{3/2})dx$$

for the function

$$\delta = -\gamma^{2/3}(\zeta_{max} - \zeta).$$

The precise universal solution is absent. It is necessary to establish the form for the size spectrum $\exp(\delta^{3/2})$ and the problem can be reduced to the algebraic equations.

æ

Determine the form of the spectrum. Under the big absolute values of Φ_{*max} the solution transforms into the already known in the frames of the linearization of the argument of the exponent on the supersaturation. This parameter is negative. One can can show that the deviations in the form of the spectrum increase when this parameter grows. Consider the case under the zero value of this parameter. Then

$$3z\int_{-\infty}^{0} (z-x)^2 \exp(\delta^{3/2})dx = \delta(z) + \int_{-\infty}^{z} (z-x)^3 \exp(\delta^{3/2})dx.$$

The numerical solution gives the spectrum with the form which practically coincides with the case under the linearization (the absence of 3/2 in the argument of the exponent)

$$3z\int_{-\infty}^{0} (z-x)^2 \exp(\delta)dx = \delta(z) + \int_{-\infty}^{z} (z-x)^3 \exp(\delta)dx.$$

The forms of the spectrums after the mentioned rescaling are drawn at the fig. 6.7. They practically coincide.

The form of the spectrum is the quasi integral of the motion along Φ_{*max} and it is now established. The problem is reduced to some set of the algebraic equations. But in these algebraic equations the power 3/2 is important. The situation is analogous to the gaussian approximation from the chapter four. The gaussian approximation is valid for

the droplets spectrum but the tail corresponding to the big droplets isn't well described. Here the situation is the same. The first iteration ensures the right determination of the conditions of the formation of the main consumers of the vapor during PIFD[23].

Certainly, the condensation can occur without barrier. Here the solution will be extremely simple. The already obtained form of the spectrum has to be taken for $z < z_{00}$ where z_{00} corresponds to the disappearing of the activation barrier. Then one can get $\eta(z_{00})$ and add to the spectrum the delta function $\delta(z_{00})\eta(z_{00})$. At $z > z_{00}$ one has to put the spectrum to zero.

One has also to investigate the properties of the solution which form the base of the mathematical model of the given system of equations.

The general features of the condensation process

Earlier the mathematical model was based on some properties as the macroscopic description of the critical embryo. Now we can show that these properties are necessary for the condensation as the physical phenomena. In other words these features are responsible for the possibility of the observation of the condensation.

Note the characteristic features of the solution used in the construction of the mathematical model

- (A)

  The value g_*/Φ_* is small.

- (B)

  The relative variation of the ideal supersaturation during PIFD $\Delta\Phi/\Phi_*$ is small.

- (C)

  The quasi stationary state is valid for the near critical embryos during PIFD.

- (D)

  The role in the vapor formation is played by the super critical embryos which are growing regularly.

In the case of the homogeneous condensation the properties (A)-(D) are justified analytically and are based on $F_c \sim \frac{a}{3}\Gamma^{2/3}$, $\Gamma \sim \nu_c \gg 1$.

[23] When the power 3/2 is substituted by the infinite value under the known amplitude of the supersaturation we come to the situation of the decay where the consideration is absolutely analogous.

After the solutions are obtained one can reformulate these properties. It follows that $g/\Phi \sim 1/\Gamma$ and $\Delta\Phi/\Phi \sim 1/\Gamma$. The inequalities corresponding to the properties (A) and (B) have the same power.

All properties are essential for the construction of the solution of the kinetic equation. The property (A) together with (B) is necessary to apply the exponential approximation in the balance equation. Certainly, the Bolzman distribution is also necessary. The property (B) is necessary for the possibility of the linearization of the ideal supersaturation during PIFD.

The property (A) ensures the possibility to observe the process of the condensation as the physical phenomena. The process of the phase transformation has two evident finals - the asymptote of Lifshiz-Slezov or the delta like spectrum. Here practically all information about the condensation is absent. Consider the pseudo homogeneous situation where the quantity of the substance in the droplets is the maximal. One can speak about the finish of the nucleation only when the system come to the new period with the new integrals of the evolution. The number of the droplets is one of these integrals. The necessary condition is the conservation of this number.

The sharp character of the consumption of the vapor by the droplet is responsible for the rapid convergence of the iterations.

To observe the result of the nucleation the duration of the period with the simplified evolution must be longer than PIFD (which due to the property (B) is rather short). When the whole surplus substance is in the droplets the process is going to transform into the coalescence. The avalanche character of the vapor consumption[24] by the droplet leads to the fact that **the relative smallness of the substance in the droplets is the necessary condition to observe the result of the droplets formation.**

When the property (B) is violated then the nucleation transforms into the coalescence practically simultaneously.

The properties (A), (B) have no connection with the appearing of the embryos. They are responsible for the global structure of the phase transformation. The properties (C), (D) are connected with the appearing of the super critical embryos. In the heterogeneous condensation one can imagine some situations where these properties are violated. But in the homogeneous condensation they can be derived from (A).

When the height of the activation barrier in the heterogeneous condensation is small, then Γ goes to zero and the properties (A), (B) dis-

[24]This property can not disappear after the end of PIFD until the coalescence.

appear. The possibility to observe the nucleation as some period leading to the completed effect disappears also.

* * *

The properties (A), (B) are necessary for the condensation as the physical phenomena. The properties (C), (D) depend of the form of the near critical region. Are they really necessary?

The universal form of the spectrum is based on the following two properties

- (*)

  The applicability of the exponential approximation on the front side of spectrum.

- (**)

  The avalanche character of the vapor consumption.

To establish the universal form one need only the functional dependence in the form of the exponent (not the quasi stationary approximation).

According to [65] under the stationary value of $n \sim \partial F_c/\partial t$ one can see the specific rate of the nucleation with the exponential form and some renormalizing factors.

Due to the avalanche character of the vapor consumption and the property (B) the parameter n is constant at the front side of the spectrum. It allows to get the same form of the spectrum associated with the behavior of the supersaturation[25] as in the stationary case. This form is associated with the behavior of the supersaturation (not with the rate of nucleation). But it is the direct base for the final results which solves the self consistent problem.

When the rate of nucleation increases the value of n decreases and the intensity of the nucleation increases. This makes the convergence of the iterations even more rapid. Then the first iteration will be a rather good approximation for the form of the spectrum.

When the analytical expansion for the free energy doesn't have the negative value of the second derivative on ν for all values of ν then the coagulation is possible. This changes the previous expression for the rate of nucleation in thousands of times. But the exponent form of the expression for the rate will take place in this case also. Instead

[25] The final form will be the other as far as n will be changed.

of one factor $\exp(-F_c)$ there will be one (or several) pair of factors $\exp(-F(\nu_1))\exp(-F(\nu_2))$, where $\nu_1 + \nu_2 > \nu_c$ and $F(\nu_1) + F(\nu_2)$ attains minimum. The Zeldowitch factor will be another but it is unessential. The equilibrium distribution for ν_1 and ν_2 is valid. The kinetic factor is the weak function of the supersaturation. Then the necessary approximation is evident.

In the previous constructions the avalanche character of the vapor consumption was the consequence of the regular law of growth. Now we are going to show that this property takes place even when the ensemble of the embryos is in the near critical region.

In the near critical region we can consider only the diffusion of the embryos.

The big value of the near critical region requires the small value of the derivative of the free energy on ν. Then the embryo in the near critical region perturbs the environment weakly. Then the regime of the vapor consumption will be the free molecular one. Then the natural variable will be the linear size of the embryo. It is extracted by the fact that the intensity of the elementary interactions multiplied on the elementary variation of this variable in the elementary act doesn't depend on the concrete value of this variable.

The boundary condition will be some constant on time at the critical size. The solution will be the superposition of the Green functions. Then one has to write the Green function of the diffusion equation in this variable. Then one can found the average number of the molecules inside the embryo and see that it grows as the time in the power 3/2 (instead of 3 under the regular growth)[26]. This power formally corresponds to the diffusion regime of the vapor consumption. As we know the avalanche character will be observed here. The first iteration is a good approximation for the form of the spectrum.

The power of the nonstationarity n can not be too big. It can be seen from the requirement to observe the condensation as the phenomena. The rate of the decrease of the supersaturation on the back side of the spectrum is higher that the increase at the front side. But the value $n = -1$ corresponds to the situation when the critical embryo moves with the same velocity as the velocity of the regular growth. It means that the coalescence begins. Here the connection between the low nonstationarity and the condensation as the physical phenomena is observed.

Now all requirements are reduced to the three ones:

[26]The decrease of the number of the embryos isn't important because in the frames of this formalism this number is determined by the other way.

- the condensation can be observed,
- the avalanche character of the metastable phase consumption,
- the Bolzman form of the equilibrium distribution of the embryos.

The last requirement is the necessary condition to speak about the embryo as the object (the quasi isolated object). The free energy is the smooth function of the external parameters. It is important together with the Bolzman distribution.

What is supposed under the conception of the embryo? The embryo is some developing object. It corresponds to the increasing size of the embryo, the increasing rate of the metastable phase consumption. As the result the avalanche character of the consumption is associated with the conception of the embryo as the developing object. The second requirement is, thus, also the terminological one. The universal distribution is justified now for the general process of the condensation.

6.6 Condensation with the source of the heterogeneous centers

The total number of the free heterogeneous centers will be marked by η. The balance equation will be the following

$$\frac{d\eta}{dt} = J_+ - J - J_-,$$

where J is the intensity of the droplets formation, J_- is the intensity of the recombination, J_+ is the intensity of the source of the heterogeneous centers. We suppose J, J_- and J_+ to be positive.

The functions J, J_- and J_+ are rather complicate and may be not so well known. But the dependence on η is rather simple

$$J \sim \eta, \quad J_+ \sim const, \quad J_- \sim \eta^2.$$

The value of η_{st} is the stationary number of the heterogeneous centers and is determined from the equation

$$J_+ = J(\eta_{st}) + J_-(\eta_{st}).$$

The value η_{st}^0 can be considered as the initial value for the nucleation process. It is determined from

$$J_+ = J_-(\eta_{st}^0).$$

One can show that until the maximum of the supersaturation

$$\eta > \eta_{st}.$$

To see the dependence of J on the supersaturation one can prove the following statements

Statement 1

The leading term in the dependence of J on the supersaturation is the Bolzman factor $\exp(-\Delta F)$.

The justification is based on the special form of the kinetic equation for the function $f(x)/\exp(-\Delta F)$ after the Laplace transformation. As far as this equation for the function $f(x)/\exp(-\Delta F)$ doesn't contain the sharp dependencies and the bifurcation points[27] then this statement is evident.

Then one can prove the following

Statement 2

For $d^2\Phi/dx^2 \leq 0$ after the maximum of the supersaturation when

$$z - z_{max} \sim (\frac{4\zeta_{max}}{f_{max}\Gamma(\zeta_{max})})^{1/4} \equiv \Delta_{nat},$$

then

$$f(z) \leq \frac{f_{max}}{\exp(1)}.$$

The index "max" marks the values at the maximum of the supersaturation.

The justification follows from the positive value of the second derivative of the substance in the droplets on time and the consideration analogous to the decay of the metastable state.

Extract the smooth and the sharp dependencies on the supersaturation ζ. The function J/η is the sharp function of the supersaturation ζ; the functions J_-/η^2 and J_+ are the smooth functions of ζ.

Introduce the characteristic value ζ_{thr} according to

$$J(\zeta_{thr}, \eta^0_{st}) \sim J_+.$$

6.6.1 Quantitative description

Solve the problem with the fixed total number of the heterogeneous centers η^0_{st}. Then one can get the supersaturation ζ_{fix} during PIFD and

[27] Also in the boundary conditions.

the value of

$$h(\zeta_{fix}) = \frac{6\Gamma(\zeta_{fix})\eta^0_{st}}{\zeta_{fix} n_{*\infty} c^3(\zeta_{fix})},$$

where

$$c = \frac{\zeta}{\Gamma}\frac{d\Phi}{dx}.$$

There will be the three situations.

A.$h \gg 1$.

The process is the pseudo homogeneous one. The action of the source can not be observed.

B.$h \ll 1$.

The action of the source is important. One has to calculate ζ_{thr}. There are three subsituations.

B1. $\zeta_{fix} - \zeta_{thr} \gg \zeta_{thr}/\Gamma(\zeta_{thr})$.

Until $\zeta < \zeta_{thr}$ one has $\eta = \eta^0_{st}$ and there is no action of the source. After ζ becomes greater than ζ_{thr} the number of the already existed heterogeneous centers is so great that it can not be exhausted until the intensity of the exhausting will be that attained at ζ_{fix}. Until ζ_{fix} the number of the heterogeneous centers is near η^0_{st} and the action of the source can not be observed.

Meanwhile after ζ attains ζ_{fix}, as far as $h \ll 1$, the supersaturation continues to grow. It means that J/η grows very rapidly. The only way to avoid the negative values of η which are forbidden is the vanishing of η. Then $\eta \ll \eta^0_{st}$.

The last inequality produces some important consequences. From the balance equation it follows that approximately

$$J = J_+.$$

Hence, we know the intensity of the formation of the droplets. Due to $h \ll 1$ the supersaturaturation continues to grow at least several $\Delta_{nat}\tau/\zeta$. Rather soon after $t(\zeta_{fix})$ we can consider that near ζ_{fix} the monodisperse spectrum with η^0_{st} droplets was formed.

To reconstruct the spectrum we have to establish the dependence $\zeta(t)$. As far as we consider that the deviation of ζ_{max} from ζ_{thr} isn't

essential the problem of the height of the tail of the spectrum doesn't appear.

We shall put t_* to $t(\zeta_{fix})$ $(t < t(\zeta_{max}))$. For the function $\zeta(z)$ we have the following evident equation

$$\Phi(z) = \zeta(z) + \eta^0_{st} z^3 + \int_0^z (z-x)^3 \frac{J_+\tau}{\zeta_{thr}} dz.$$

The integral in this equation can be easily calculated.

For the constant J_+ we have

$$\zeta(z) = \Phi(z) - \eta^0_{st} z^3 - \frac{z^4}{4} \frac{J_+\tau}{\zeta_{thr}}.$$

The only thing we need from the last equation is the end of the tail of the spectrum. Certainly, the spectrum will come to the end when the supersaturation falls down to ζ_{thr}. So, we have a simple expression

$$\zeta_{thr} = \Phi(z_{fin}) - \eta^0_{st} z^3_{fin} - \frac{z^4_{fin}}{4} \frac{J_+\tau}{\zeta_{thr}}$$

for z_{fin}, i.e. for the end of the spectrum. The spectrum contains the monodisperse head with η^0_{st} droplets and the tail with the height $\frac{J_+\tau}{\zeta_{thr}}$ and the length z_{fin}. We shall speak about such a spectrum as about "the long spectrum".

B2.$-\zeta_{fix} + \zeta_{thr} \gg \zeta_{thr}/\Gamma(\zeta_{thr})$.

For $\zeta < \zeta_{thr}$ the number of the free heterogeneous centers is equal to η^0_{st}. We have to calculate the pseudo homogeneous version of the process. We shall keep $\eta = \eta^0_{st}$ and calculate the result of the process by the known procedure of disbalanced iterations when $h \gg 1$. As the result we can find the characteristic supersaturation ζ_{hom} of the formation of the pseudo homogeneous spectrum.

We have three opportunities.

B2-1. $-\zeta_{hom} + \zeta_{thr} \gg \zeta_{thr}/\Gamma(\zeta_{thr})$.

In this case we have the real pseudo homogeneous condensation. Here $max\ \zeta = \zeta_{hom}$. All results of the description of the homogeneous condensation can be applied.

B2-2. $\zeta_{hom} - \zeta_{thr} \gg \zeta_{thr}/\Gamma(\zeta_{thr})$.

Here we have the same situation as in the case B1 (with the substitution ζ_{fix} by ζ_{thr}).

B2-3. $\zeta_{hom} \sim \zeta_{thr}$.

Mark by $z = 0$ the point where $\Phi = \zeta_{hom}$.

If $\zeta_{thr} \leq \zeta(z = -3/2c) \approx \Phi(-3/2c)$ then there is the exhaustion of η and, thus, the situation of the "long spectrum". The difference is that the "tail" is rather short and instead of the monodisperse approximation we have to use the true expression with the four initial moments of the spectrum.

If $\zeta_{thr} \geq \zeta(z = -3/2c) \approx \Phi(-3/2c)$ then the behavior of the supersaturation is known. Really, the validity of the expressions obtained on the second step of the iteration procedure is based on the fact that the main consumers of vapor are born at $z \approx -3/c$. Here we know that the characteristics at $z = -3/c$ are the pseudo homogeneous ones and the solution for the supersaturation is the pseudo homogeneous one.

B3. $\zeta_{fix} \approx \zeta_{thr}$.

As far as $h \ll 1$, the supersaturation continues to grow after it attains ζ_{fix} (and ζ_{thr}). Soon after it attains these values we have $\eta \ll \eta^0_{st}$ and, hence, the situation with the "long spectrum".

C. $h \sim 1$.

Calculate ζ_{thr}. We also have three opportunities.

C1. $\zeta_{fix} - \zeta_{thr} \gg \zeta_{thr}/\Gamma(\zeta_{thr})$.

The action of the source of the heterogeneous centers disappears. So, the situation is reduced to the already known ones.

C2. $\zeta_{thr} - \zeta_{fix} \gg \zeta_{thr}/\Gamma(\zeta_{thr})$.

The number of the free heterogeneous centers is known, it is equal to $\eta = \eta^0_{st}$. So we can use the pseudo homogeneous description of the condensation.

C3. $\zeta_{thr} \approx \zeta_{fix}$.

This situation has three opportunities.

C3-1. $\zeta_{hom} - \zeta_{thr} \gg \zeta_{thr}/\Gamma(\zeta_{thr})$.
This situation can not take place.

C3-2. $\zeta_{thr} - \zeta_{hom} \gg \zeta_{thr}/\Gamma(\zeta_{thr})$.
The number of the free heterogeneous centers is known, it is equal to $\eta = \eta_{st}^0$. So, we can use the pseudo homogeneous description of the condensation.

C3-3. $\zeta_{thr} \approx \zeta_{fix}$.
This situation is the principally intermediate one.

In the next section we shall formulate some new ideas which are necessary to solve this situation as well as the situation with $h \ll 1$, $\zeta_{fix} \sim \zeta_{thr}$ (note that we know only the behavior of the supersaturation in this situation).

6.6.2 Universal spectrum

The various situations of the condensation process have some common features. The leading idea formulated earlier was the idea of the universal spectrum. Contrary to the homogeneous condensation the heterogeneous case with one sort of the fixed number of centers has no universal form of spectrum. But we have to notice that the resulting formula for the number of the heterogeneous centers (and, thus, for the number of the droplets - the main characteristic of the process) is based on the universal spectrum $\exp(x - \exp(x))$.

We have noticed that all limit cases can be reduced to some modifications of the universal solution method or to the situation of the long spectrum.

Here we shall check whether the ideas of the universal spectrum can be applied in this situation. Now we know that it can be done if we can reduce the problem under consideration to the some model problem with the fixed number of the centers. Certainly, the parameters of the process will be the different ones.

The initial problem can be written in the following manner

$$\frac{d\theta}{dt} = -b\exp(\varphi)\theta - c(\theta^n - 1), \tag{6.6.17}$$

$$\varphi = z - a\int_{-\infty}^{z} (z-x)^3 \exp(\varphi)\theta dx \tag{6.6.18}$$

for the functions

$$\varphi = \frac{\Gamma(\Phi_*)}{\Phi_*}(\zeta - \Phi_*), \tag{6.6.19}$$

$$\theta = \frac{\eta}{\eta^0_{st}} \tag{6.6.20}$$

and the letters a, b, c mark some parameters of the process[28].

The power n is supposed to be the integer parameter with the values $n = 1$, $n = 2$. The value $n = 2$ corresponds to the ordinary intensity of recombination in the ideal gas. The value $n = 1$ appears after the linearization over η. Really, $\eta \leq \eta^0_{st}$. When $\eta \ll \eta^0_{st}$, the action of recombination is negligible. So, the linearization is quite reasonable.

This system can be applied to the formation of the first part of the spectrum, i.e. the "head" of the spectrum. May be it is necessary to consider the formation of the "tail" of the spectrum. Later we shall give the qualitative estimates how to extract the "head" and the "tail" of the spectrum.

The value of t_* can be chosen as the moment during the period of formation of the "head" of the spectrum. If we can approximate the current situation by the model problem, we can use any of the possible ways to extract t_* in the model situation.

We shall consider the following model problem

$$\frac{d\theta}{dt} = -b_0 \exp(\varphi)\theta, \tag{6.6.21}$$

$$\varphi = z - a_0 \int_{-\infty}^{z} (z - x)^3 \exp(\varphi)\theta dx \tag{6.6.22}$$

with some other parameters a_0 and b_0.

The solution of the last problem on the base of the universal spectrum is known.

We have to declare the way how to determine a_0, b_0 on the base of a, b, c.

The choice of t_* leads to some errors in the approximations for the intensity of the droplets formation. When $b_0 \gg a_0$, the result of the process is obvious - all the centers are in the droplets. So, one has to ensure the precise description in the opposite situation. Hence, one can take t_* as the moment of the maximum of the intensity of the droplets formation in the pseudo homogeneous situation. This leads to $a_0 \approx 1/6$

[28]The linearization of the ideal supersaturation is done.

(calculated in the first iteration). The same construction leads to $a \approx a_0 \approx 1/6$. Now we have to consider b, c and b_0.

The most representative part of the spectrum is near the maximum. So we shall put the maximum of spectrum in the initial problem and in the model problem to one and the same point. Let us find these points.

For the initial problem the simplest solution is the following one. The spectrum is described by the function

$$S = \theta \exp(\varphi). \tag{6.6.23}$$

Then

$$\frac{d}{dx}\theta \exp(\varphi) = \frac{d\theta}{dx}\exp(\varphi) + \frac{d\varphi}{dx}\theta \exp(\varphi). \tag{6.6.24}$$

For $\frac{d\theta}{dx}$ we have (6.6.17), the analogous derivative $\frac{d\varphi}{dx}$ has to be defined from the universal spectrum

$$\exp(\varphi) = \exp(x - \exp(x)). \tag{6.6.25}$$

For the model problem the analogous expressions are the following

$$S = \exp(x - \kappa \exp(x)), \tag{6.6.26}$$

where κ is the parameter of maximum. The last expression is written on the base of the universal spectrum which is justified for the model problem - the problem with the fixed number of the heterogeneous centers. We have

$$\exp(\varphi) = \exp(x - \exp(x)), \tag{6.6.27}$$

$$\theta = \exp(-(\kappa - 1)\exp(x)). \tag{6.6.28}$$

The differentiation gives the position of the maximum

$$x = -\ln(\kappa). \tag{6.6.29}$$

Now we have to establish the position of the maximum in the initial problem. The differentiation gives

$$\frac{dS}{dx} = (-b\exp(x - \kappa\exp(x)) - c(\exp(-n(\kappa - 1)\exp(x)) - 1)) \tag{6.6.30}$$
$$\exp(x - \exp(x)) + (1 - \exp(x))\exp(x - \kappa\exp(x)).$$

The maximum must be attained at $x = -\ln(\kappa)$ and

$$\frac{dS}{dx} \mid_{x=-\ln(\kappa)} = 0. \tag{6.6.31}$$

The direct substitution leads to the following equation

$$(\frac{b}{\kappa}\exp(-1) + c(\exp(-n\frac{\kappa-1}{\kappa}) - 1))\exp(-\frac{1}{\kappa}) = (1-\frac{1}{\kappa})\exp(-1). \tag{6.6.32}$$

This equation gives the value of κ which leads to b_0 according to

$$b_0 = \kappa - 1. \tag{6.6.33}$$

The numerical calculations will prove the required reduction. The reduction of the current problem to the problem with the fixed number of the heterogeneous centers allows to use the characteristic lengths of the last process. Namely, we have to introduce the concrete cut off of the head of the spectrum. We shall cut the spectrum at the moment when the 95 percents of the droplets in the modified problem are already formed. We shall calculate this number in the second iteration. The last number corresponds to the normal accuracy of the iteration procedure.

Now we can turn to the numerical calculations.

Let us put $n = 1$. The table 1 demonstrates the relative error of the second iteration of the modified model in comparison with the precise numerical result taken in percents.

Let us put $n = 2$. The table 2 demonstrates the relative error of the second iteration of the modified model in comparison with the precise numerical result taken in percents.

As the result we see that the relative error is rather small and is in the frames of the characteristic experimental error. The problem to consider now is connected with the behavior of the relative error for the big values of c. We see that the relative error of the precise result of the model problem is very small. The table 3 shows the error in percents for $n = 1$ and the table 4 shows the error for $n = 2$.

So the relative error of the second iteration is rather small and corresponds to the analogous error in the case of the initial problem with the fixed number of the heterogeneous centers.

We see that our idea about the possibility of description with the help of the universal spectrum is rather productive. It can lead to the relatively precise description of the problem under the consideration[29].

[29]The relative deviation grows with the growth of z. Then the deviation in the local sense is also small. It allows to use the standard theory of perturbations.

c	b						
	0.125	0.25	0.5	1	2	4	8
0	8.99	6.01	0.473	−8.40	−17.6	−18.8	−11.4
0.125	9.56	7.15	2.74	−4.21	−10.8	−11.9	−10.0
0.25	9.98	8.00	4.36	−1.27	−6.53	−6.47	−7.41
0.5	10.56	9.12	6.52	2.50	−1.29	−0.023	−1.05
1	11.17	10.31	8.75	6.29	3.77	4.75	8.26
2	11.63	11.21	10.43	9.15	7.62	7.60	12.1
4	11.89	11.71	11.38	10.79	6.96	9.42	11.35
8	12.0	11.93	11.79	11.54	11.13	10.66	10.85

Table 6.1: The relative error of the second iteration of the modified model in comparison with the precise numerical result taken in percents for $n = 1$

c	b						
	0.125	0.25	0.5	1	2	4	8
0	–	–	–	–	–	–	–
0.125	9.96	7.92	4.08	−2.24	−9.21	−11.43	−9.84
0.25	10.54	9.04	6.24	1.49	−4.07	−5.65	−6.80
0.5	11.15	10.25	8.85	5.59	1.75	0.051	0.28
1	11.63	11.19	10.35	8.85	6.70	5.47	7.80
2	11.89	11.71	11.35	10.70	9.68	8.72	10.09
4	12.01	11.93	11.79	11.52	11.07	10.49	10.56
8	12.06	12.02	11.96	11.85	11.64	11.32	11.04

Table 6.2: The relative error of the second iteration of the modified model in comparison with the precise numerical result taken in percents for $n = 2$

c	b						
	0.125	0.25	0.5	1	2	4	8
4	−0.10	−0.34	−0.78	−1.55	−2.69	−3.52	−0.9
8	0.03	−0.07	−0.26	0.6	−1.19	−1.92	−1.9

Table 6.3: The relative error of the precise solution of the modified model in comparison with the precise numerical result taken in percents for $n = 1$

c	b						
	0.125	0.25	0.5	1	2	4	8
4	0.030	0.068	0.26	-0.63	-1.27	-2.14	-2.25
8	0.086	4.54	-0.038	-0.20	-0.50	-1.00	-1.54

Table 6.4: The relative error of the precise solution of the modified model in comparison with the precise numerical result taken in percents for $n = 2$

The current description in the intermediate case is based on the natural suppositions about the validity of the quasi stationary distribution in the near-critical region and about the regular post-critical character of the growth of the main consumers of the vapor during the period of the formation of the spectrum. These assumptions can be directly checked. When they are violated then they are not important.

6.6.3 Condensation with the absence of recombination

The last situation we have to describe is the situation with the absence of recombination.

Note that for the condensation with the fixed number of the heterogeneous centers one can see that the duration of PIFD Δt is very small in comparison with t_* chosen as the characteristic moment of this formation. So the action of the source during PIFD is negligible. So, we can solve the problem with the quasi stationary η_{tot}, defined as

$$\eta_{tot} = \int_{z_{st}}^{z} dx A(x),$$

where A is the intensity of the source in the scale z, x, z_{st} is the moment when the source of the centers starts to work and the initial value of centers is supposed to be zero (the modification is trivial). The generalization is evident. One can apply the methods of the second chapter and get the result. In the intermediate calculations the parameter h is appeared. The result will be the final one for all $h \geq 1$. Only in the situation $h \ll 1$ one have to add the long tail of the spectrum. The situation is quite analogous to the situation with the "long spectrum". It can be solved by the same procedure.

6.7 Condensation in the spatially unhomogeneous systems

The wide spread example of the unhomogeneous system is the diffusion chamber [38]. We are going to prove the existence of the universal spectrum also in this case. So, there is no need to consider the technical details of the chamber.

Earlier the theory was constructed only for the collective regime of the vapor consumption [36] without the determination of the form of the spectrum.

6.7.1 The consumption of the vapor by the separate droplet

The theory will be constructed only for the action on the density of the vapor. The action on the temperature of the vapor can be included in the standard way.

The vertical direction will be marked by h. The Stocks law will be used for the stationary velocity of the droplets fall

$$(\frac{dh}{dt})_{st} = K\rho^2 \tag{6.7.34}$$

with the characteristic constant[30] K, where

$$\rho = \nu^{1/3} \tag{6.7.35}$$

and ν is the number of the molecules inside the droplet. Then ρ is the linear size of the droplet.

One can show that the quasi stationary approximation is valid.

To simplify the theory we shall consider the free molecular consumption of the vapor. It allows to consider both the case without the profiles of the density and the case with the profiles of the density. For the velocity of the droplets growth one can get

$$\frac{d\nu}{dt} = K\rho^2, \tag{6.7.36}$$

where K is some constant. Later all known constants will be marked by K.

[30] The dependence of this constant on the supersaturation is rather weak in comparison with the rate of nucleation. The vapor consumption doesn't essentially perturb the velocity of the droplet fall and the rate of the droplet growth.

Then one can come to

$$\frac{dh}{dt} = K\frac{d\nu}{dt}, \tag{6.7.37}$$

or

$$\frac{d\nu}{dh} = K. \tag{6.7.38}$$

This equation forms the base for to neglect the diffusion along h for the profile of the separate droplet.

One can show that

- The profile of the rate of nucleation has essentially sharp character[31].
- One can use the ordinary macroscopic law for the intensity of the vapor consumption.

The profile of the intensity of the formation around the given droplet can be well approximated by the cylinder. It follows from the consideration analogous to the consideration in the chapter five.

The radius of such cylinder is given by the formalism of the Green functions. It isn't so necessary to determine this profile in the accurate form because it is going to dissipate in time. The situation is approaching to the collective regime of the vapor consumption.

The last equation shows that the diffusion along h is small. Then one can solve the plane problem instead of the spatial[32]. There is some weak diffusion due to the dissipation of the profiles but this diffusion can be neglected.

The diffusion from the bottom of the cylinder exists but can be also neglected.

6.7.2 The global evolution

All functions are the functions of h. The intensity of the vapor consumption jdh at the elementary interval dh is known and in the ordinary approximation it is given

$$j \sim \int_{-\infty}^{z} \exp(K(n(x) - n_{id,*}))dx, \tag{6.7.39}$$

[31] When the droplet is in this layer. Later the dissipation of the profile can be observed.

[32] The intensity of the vapor consumption is known and the situation is analogous to the chapter five.

where n is the density, n_{id} is the unperturbed value of n and $*$ marks some characteristic spatial point analogous to the characteristic moment during PIFD. All ordinary estimates can be justified[33]. One can prove[34] the quasi stationary approximation for the intensity of the vapor formation and the statement that the main role in the vapor formation is played by the super critical embryos.

As far as the diffusion equation is the linear one it can be directly written for the deviation Δn of the density n from the unperturbed value n_{id}. The stationary equation has the form

$$D\frac{\partial^2 \Delta n}{\partial h^2} \sim j, \tag{6.7.40}$$

where D is the diffusion coefficient. Having integrated this equation two times with the evident boundary conditions $n \to n_{id}$ when $z \to -\infty$ and $\partial n/\partial z \to \partial n_{id}/\partial z$ when $z \to -\infty$ one can come to

$$\Delta n = -K \int_{-\infty}^{z} (z-x)^2 \exp(K(n(x) - n_{id,*}))dx. \tag{6.7.41}$$

Due to the sense of Δn with the help of the linearization one can get

$$n_{id} = n_{id,*} + Kz. \tag{6.7.42}$$

The coefficient in front of z can be canceled by the renormalization.

The substitution of the last equation into the previous one leads to the equation from the second chapter with $n = 2$ in the homogeneous limit.

The universal form of the size spectrum will be observed for some other more complicate kernels. The property of the stability of the universal form of the spectrum is extremely important here.

6.7.3 Approximate description

To get (6.7.37) one has to use the free molecular regime of the vapor consumption. Now consider the opposite regime (diffusion) to estimate all possible situations. In the diffusion regime $d\nu/dt \sim K\rho$. Then $\rho \sim t^{1/2}K^{1/2}$ and $h \sim Kt^2$. Then

$$\frac{d\nu}{dh} = K/\rho, \tag{6.7.43}$$

[33] One can introduce here the variables z, x, which are analogous to the already considered situation. One can show the equivalency of z, h, x.

[34] Here and in all cases below and above to prove the statement means to give the analytical justification.

and from $\rho \sim t^{1/2}$, $h \sim t^2$ one can come to

$$\frac{d\nu}{dh} \sim t^{-1/2} \sim h^{-\alpha} \quad \alpha = 1/4, \tag{6.7.44}$$

or

$$\frac{(\frac{d\nu}{dh})_{h=h_a}}{(\frac{d\nu}{dh})_{h=h_b}} = (\frac{h_b}{h_a})^{\alpha}. \tag{6.7.45}$$

To get the last formulas one has to use the stationary Stoks law. The stationarity of (6.7.34) is some approximation. But then the velocity will be estimated by (6.7.34) from above and the effect of the dependence of the r.h.s. of (6.7.44) will be smaller.

The cylinder of the consumption will have the varying cross section, the radius r_0 depends on h as

$$\frac{(\frac{dr_0}{dh})_{h=h_a}}{(\frac{dr_0}{dh})_{h=h_b}} = (\frac{h_b}{h_a})^{1/8} \tag{6.7.46}$$

(the vertical diffusion is unessential).

The small value of $\alpha/2$ allows to take the quasi stationary approximation which leads to the neglection of the vertical diffusion for the separate droplet.

Instead of the power 2 in the integral equation (6.7.41) we have the power 3/2 which resembles the condensation in the homogeneous space[35]. Here also the first iteration is the base for the rather precise results[36].

The stationary regime can be observed only under the condensation of the "smog" type. It means that one can find many droplets in the elementary volume. Then one has to define the elementary volume. One can suggest the spatial length h_0 of the region corresponding to the intensive formation of the droplets. It leads to the characteristic time t_0 of the existence of the droplet in this region. Then the horizontal length can be estimated as $\sqrt{Dt_0}$. The vertical length of the elementary volume is h_0 and the volume is $V_0 \sim h_0 D t_0$. One has to get the big number of the droplets in this volume. If the number is N then the fluctuations can be estimated as[37] $\sim \sqrt{N}$.

[35] According to (6.7.43) one can introduce the factor ρ^{-1} into the integral term (6.7.39). Having expressed ρ through t as $\rho \sim t^{1/2}$ one can come to the factor $t^{-1/2}$ and then after two integrations one can come to (6.7.41) with the power 3/2.

[36] On the base of the constant cross section of the cylinder one can come to the power 2. But the form of the spectrum will be approximately the same.

[37] This estimate goes from the summation of the independent variables. Here there is the strong balancing connection which can lead to the decrease of the scale of the fluctuations.

The fluctuations can not change the form of the spectrum. The situation is analogous to the action of the microscopic corrections for the free energy. The regime of the growth also can not change the form of the spectrum essentially.

* * *

The leading idea is the idea of the universal spectrum. This allows to overcome the problems of the stability and of the justification of the theoretical description.

The analytical results show the proximity of the real solutions and the solutions on the base of the first iteration. This proximity can be also shown from the fig. 8. The curve "a" corresponds to the power 3 in the integral term, the curve "b" corresponds to the power 3/2, the curve "c" is the analytical solution in the case[38] of the power 1. The curve "d" is the universal form of the first iteration. All solutions of the homogeneous space cases are between the case with the power 3 and the case with the power 3/2.

The property of the stability of the form of the size spectrum can be established also in the spatially homogeneous systems.

Even in the heterogeneous condensation under the fixed number of the centers of one sort the function of the normalized spectrum f which has the form

$$\ln(1 - \int_{-\infty}^{z} f dx) \sim 1 - \exp(-\exp(z))$$

is the universal one. The coefficient in front of this function depends on the parameters of the process.

Now the weak dependence on the microscopic corrections under the dynamic conditions can be treated as the general established fact for the first order phase transition. The stability of the form of the spectrum is also the general fact.

The solutions of the stationary problem in the spatially inhomogeneous case and of the nonstationary problem in the spatially homogeneous case have one and the same functional form. It is the universal form of the first disbalanced iteration. So the superposition will be the solution of the unhomogeneous nonstationary problem in the sense of the functional form. Now the form is known and one has only to determine

[38] Having differentiated two times one can get the differential equation of the power 2 which doesn't contain the argument explicitly. Then it can be integrated as the dynamic onedimensional system.

the parameters by the algebraic equations. The situation is analogous to the multi dimensional condensation. The technical details from [9] can be also used here.

Post critical barriers

The analysis of the dynamic conditions allows to solve the problem of the post critical barriers of the condensation. One can imagine that in the post critical region there is a local maximum at ν_{cp}. Then after ν_c and before ν_{cp} there is a local minimum[39] ν_{ep}. The embryo after it passed the near critical region comes to the size ν_{cp}. Then it has to overcome the pseudoactivation barrier with the height $\Delta_p F = F_{cp} - F_{ep}$, where $F_{cp} = F(\nu_{cp})$, $F_{ep} = F(\nu_{ep})$. May be this barrier is greater than the initial ΔF. As far as ν_c is the global maximum then

$$\Delta_p F < F_c - F_{ep}$$

and there is no inverse flow through the near critical region.

Near ν_{ep} there will be the quasi equilibrium distribution normalized on the number of the embryos $\tilde{n}$ is this region. The pseudo activation barrier is assumed to be high and this distribution is well defined. We shall call these embryos as pseudo solvatated ones. The flow J_p through the region $\nu \approx \nu_{cp}$ can be calculated analogous to the heterogeneous case. Here the role of the heterogeneous center is played by the embryo at $\nu \approx \nu_{ep}$. The consideration is absolutely analogous to the first chapter. Namely this flow will be important for the kinetics of the global process.

Consider the dynamic conditions. One can justify analytically the standard approximations and get for $\tilde{n}$ the following equation

$$\frac{d\tilde{n}}{dx} = f_* \exp(x - \frac{\Gamma}{\Phi_*} g(x)) - \tilde{n} f_{*p} \exp(dx - \frac{\Gamma_p}{\Phi_*} g(x)),$$

where f_* is the basic value of the stationary distribution connected with the real activation barrier, f_{*p} is the basic value of the stationary distribution connected with the pseudo activation barrier, Γ_p is the value analogous to Γ but for the pseudo activation barrier, d is some parameter appeared due to the difference between Γ and Γ_p. Due to the sense of Γ as $\nu_c - \nu_e$ the value of d has the order of 1.

Actually we are interested in the analysis of the initial region of PIFD where the main consumers of the vapor during PIFD are formed. Then

[39] As far as there is no precise information about the behavior of the the free energy far from the equlibrium near critical region this situation is quite possible even in the homogeneous process.

at this region due to the sense of the applicability of the second iteration as the precise approximation one can write

$$\frac{d\tilde{n}}{dx} = f_* \exp(x) - \tilde{n} f_{*p} \exp(dx). \tag{6.7.47}$$

One can easily solve this equation precisely in the analytical form. We shall give the simple estimates. Introduce

$$\tilde{n}^s = \frac{f_* \exp(x)}{f_{*p} \exp(dx)}$$

The situation $f_{*p} \gg 1$ means that every pseudo solvatated embryo will rather soon come over the pseudo activation barrier and there is no interesting effect.

In the situation $f_{*p} \ll 1$ there occurs more interesting behavior. One can give the estimate

$$\tilde{n} < \int_{-\infty}^{x} dx f_* \exp(x) = f_* \exp(x) \ .$$

Then

$$\tilde{n} \ll n^s \ .$$

Then

$$\tilde{n} \approx f_* \exp(x) \ .$$

Then the stationary distribution function at the boundary of the supercritical region is given by

$$f_{tot} = \tilde{n} f_{*p} \exp(dx) = f_* f_{*p} \exp((d+1)x)$$

Then one can repeat all the further constructions and get the same form of the spectrum.

The main feature is that there is no essential ifluence from the pseudo solvatated embryos formed at the previous moments of time. It occurs due to the avalanche character of the front (ideal) side of the spectrum due to the ideal conditions.

The intermediate situation can be solved directly on the base of the precise solution of (6.7.47) which is the linear differential equation of the first order and the integrals can be taken analitically when $d \sim 1$ (formally they are the same as for the number of the heterogeneous centers in the second disbalanced iteration). The calculations show that the form of the spectrum variates very weak.

The reproduction of the exponential form allows to consider the sequence of the activation barriers by the same procedure. Certainly, it is necessary that F_{cp} must decrease with the number of the barrier or we shall cover this barrier by the quasiequilibrium distribution.

The property of the reproduction is extremely important for the self consistency of the approach.

The situation of the decay is another. One has to cancel here $\exp(x)$ and $\exp(dx)$ and get

$$\frac{d\tilde{n}}{dx} = f_* \exp(-\frac{\Gamma}{\Phi_*} g(x)) - \tilde{n} f_{*p} \exp(-\frac{\Gamma_p}{\Phi_*} g(x)),$$

Then the picture can not be reproduced from one pseudoactivation barrier to another barrier. Here $\tilde{n}^s = f_*/f_{*p}$. In the situation $\tilde{n} \ll \tilde{n}^s$ (one has to compare $f_* \Delta x$ and $\tilde{n}^s$, where Δx is the normal lenght initiated by the kinetics without any pseudo activation barriers) one can come to

$$n \sim x$$

after the first barrier,

$$n \sim x^2$$

after the second barrier,

$$n \sim x^n$$

after n pseudo activation barriers. So, there is no reproduction of the behavior. To describe the kinetics one has to use the cut off by the supersaturation due to the sharp character of the back side of the spectrum initiated by the supersaturation even in the monodisperse situation (the worst one).

* * *

The property of the universality allows to solve the problem of the description of the kinetics under the different regimes of the vapor consumption. The different regimes can not lead to the superposition on the level of the balance equations. But the form of the first iteration is the universal for all components g_i

$$g_{i\ (1)} = g_i^0 \exp(kx)$$

with one and the same parameter k. It allows to consider the superposition of $g_{i\ (1)}$ and get the universal form of the spectrum

$$f \sim f_0 \exp(kx - (\sum_i g_i^0) \exp(kx))$$

One can consider x as the analogous to t.

There is no need to introduce the values analogous to k_a in (3.4.73). One can define k as

$$k = \frac{d\Delta F}{dt} \mid_{id}$$

(the derivative is along the trajectory corresponding the absence of the droplets formation). It is necessary for this parameter to be positive and smooth (the variation during PIFD is small).

The avalanche character can take place only for the several characteristics of the embryo. The other characteristics can be treated as the characteristics with the slow reaction. They can be presented only as some parameters in the algebraic equations. At least there is one characteristic with the avalanche character. It is the number of the molecules ν inside the embryo.

The case when there is the situation of decay for one characteristic and the dynamic conditions for the other characteristic can be solved by the following way. The decay spectrum has the approximate rectangular form. Then it will extract some region of the universal dynamic spectrum by the simple cut off. Here the form of the spectrum is also known.

The universal form of the spectrum is important for the general statistical physics. In the equilibrium statistical physics the hierarchy of the scales of the different variables ensure the hierarchy of the frequencies of the motion along these variables and the hierarchy of the distances between the energy levels. Thus, the squeezed description can be presented. The possibility of the squeezed description has the conceptual importance for the theory.

Here the squeezed description can be also attained due to the unique form of the spectrum. The result of the multi component condensation states that it is possible to neglect some variables in the process of the establishing of the form of the spectrum. Here the possibility of the squeezed description has the kinetic nature. It has here the conceptual importance also.

æ

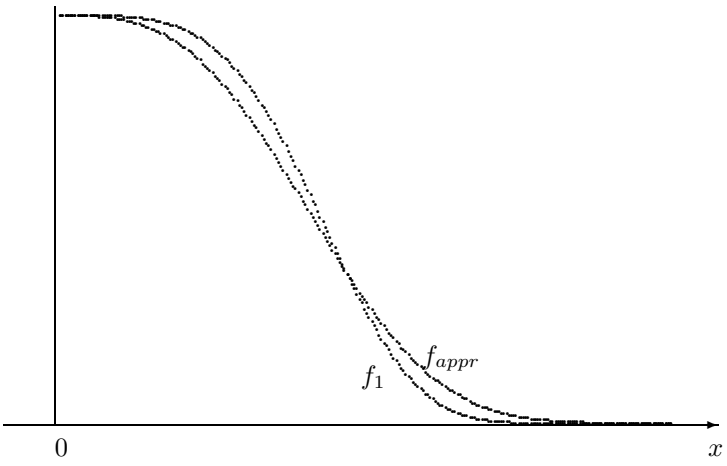

Fig. 6.1. The form of the spectrum in the monodisperse approximation.

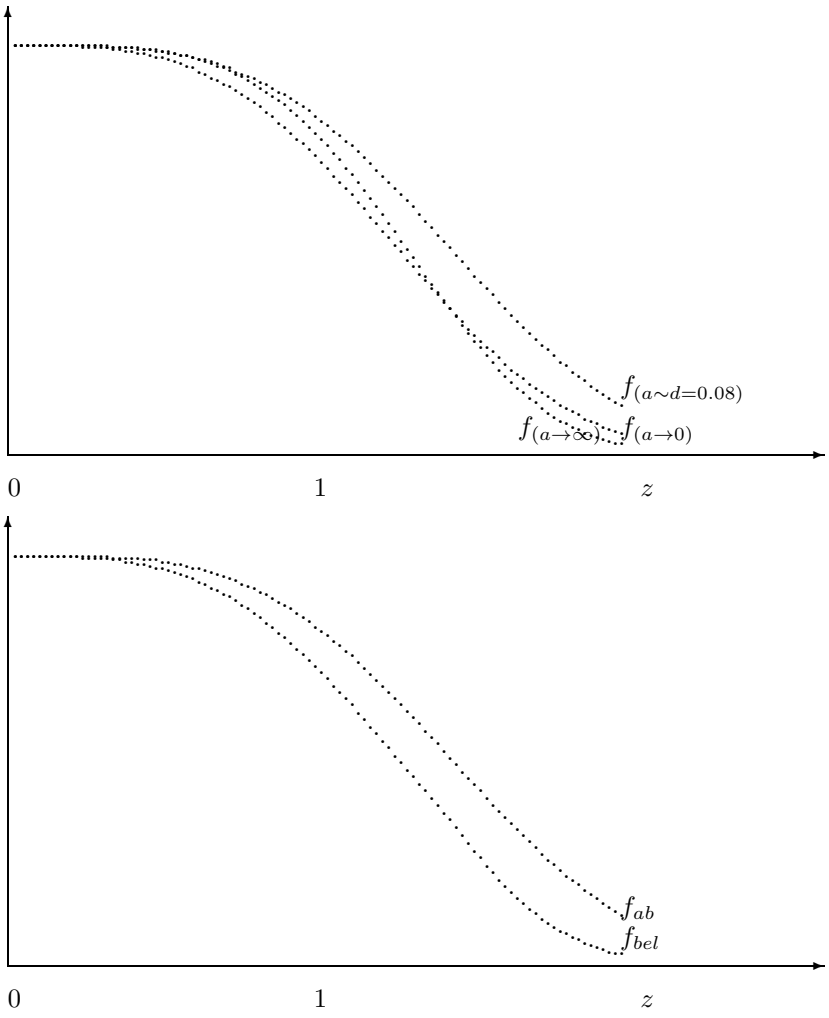

Fig. 6.2. The approximate universiality of the spectrum.

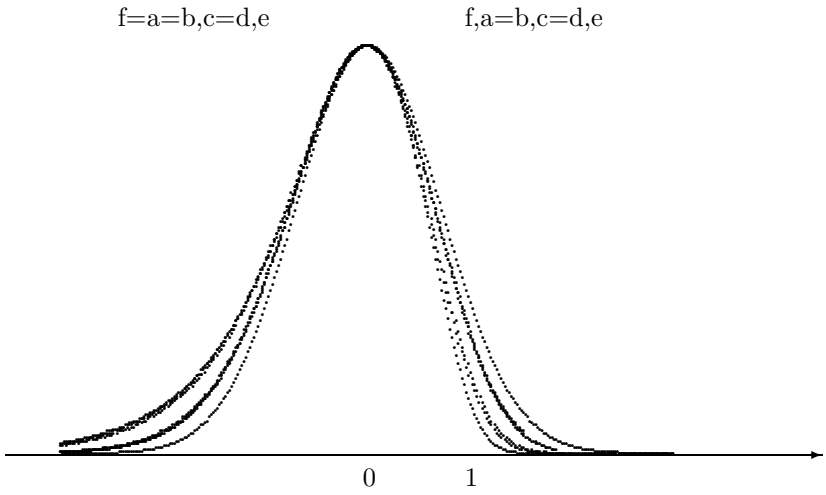

Fig. 6.3. The form of the spectrum for the different powers of the deformation.

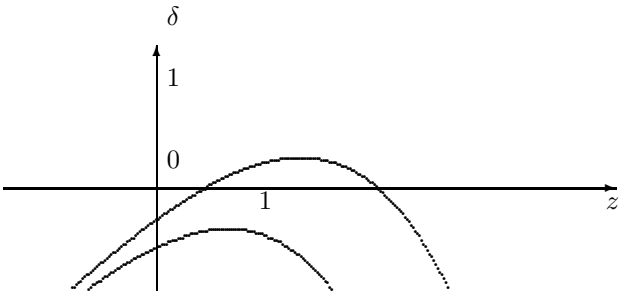

Fig. 6.4, part "a".

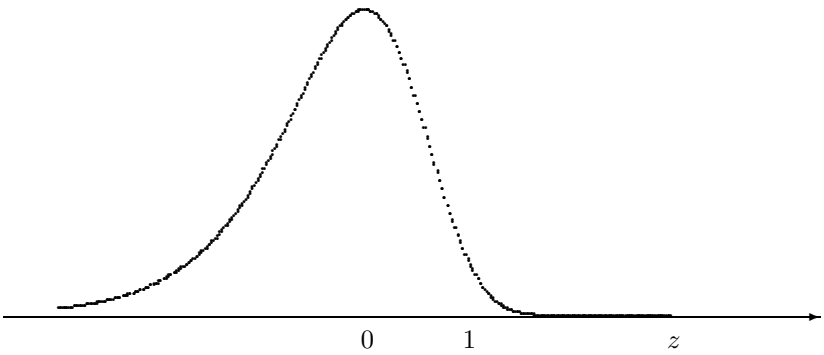

Fig 6.4, part "b"

Fig. 6.4. The weak dependence of the spectrum on the base of approximations.

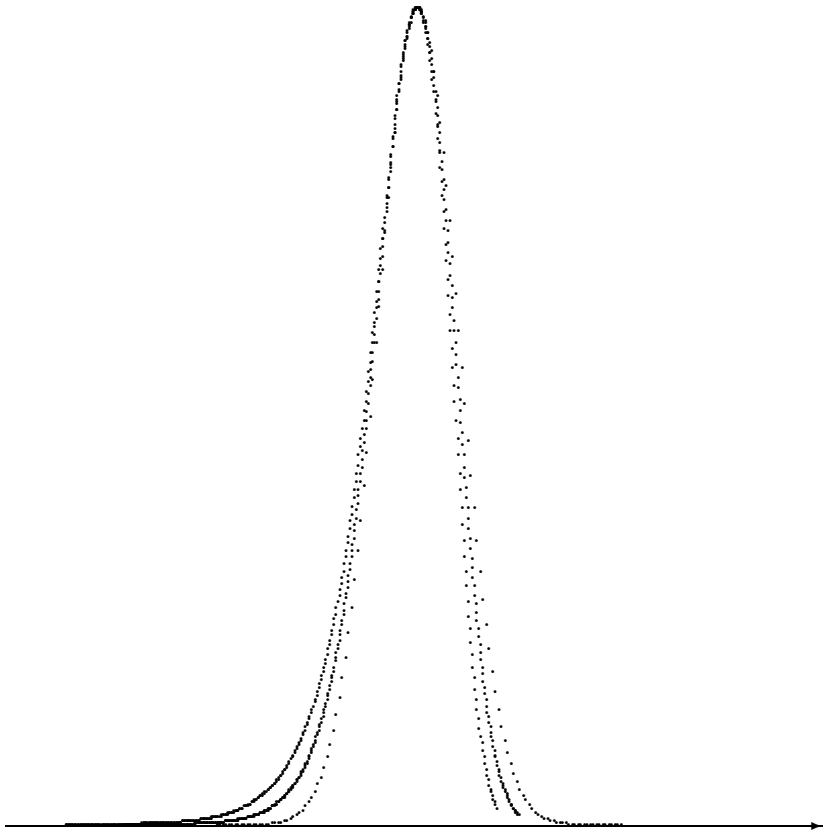

Fig. 6.5. The behaviour of the supersaturation in the condensation on one sort.

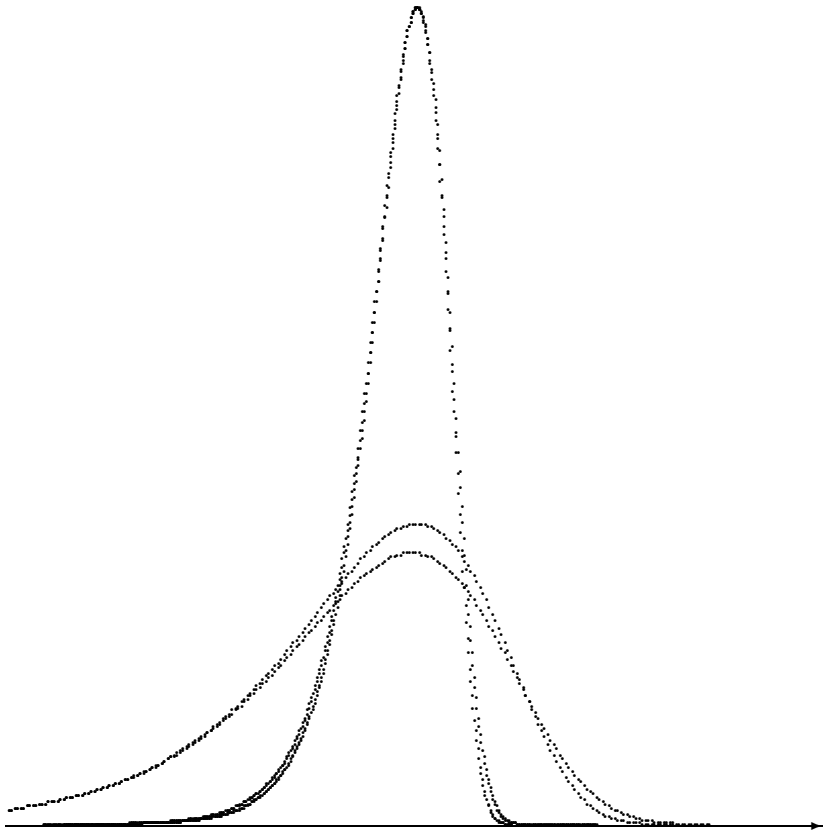

Fig. 6.6. The forms of the spectrum in the condensation on the one sort.

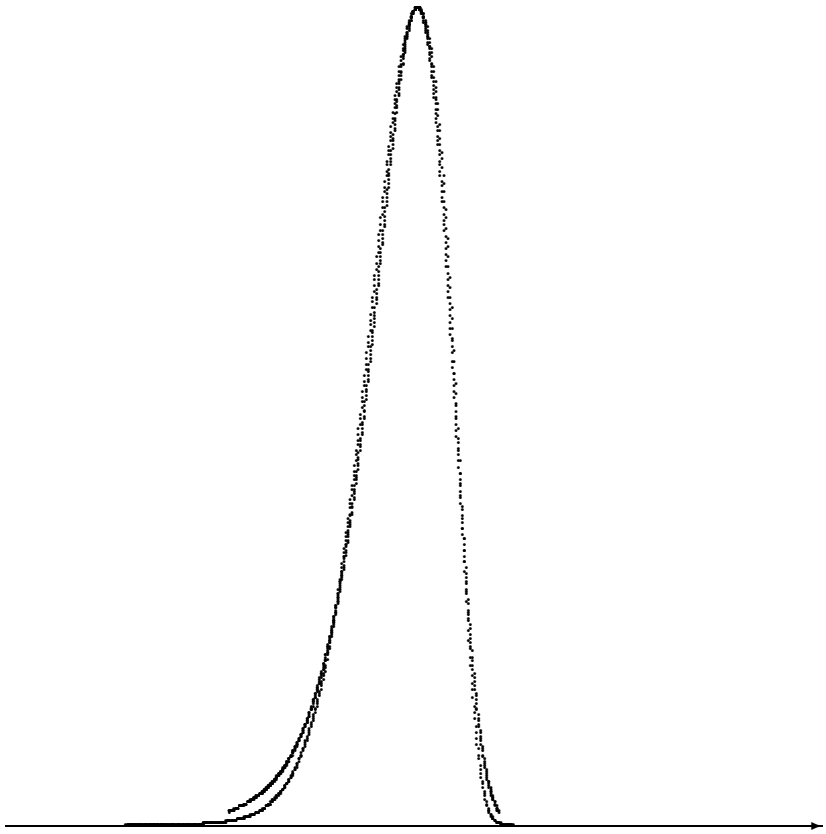

Fig. 6.7. The different forms of the spectrums.

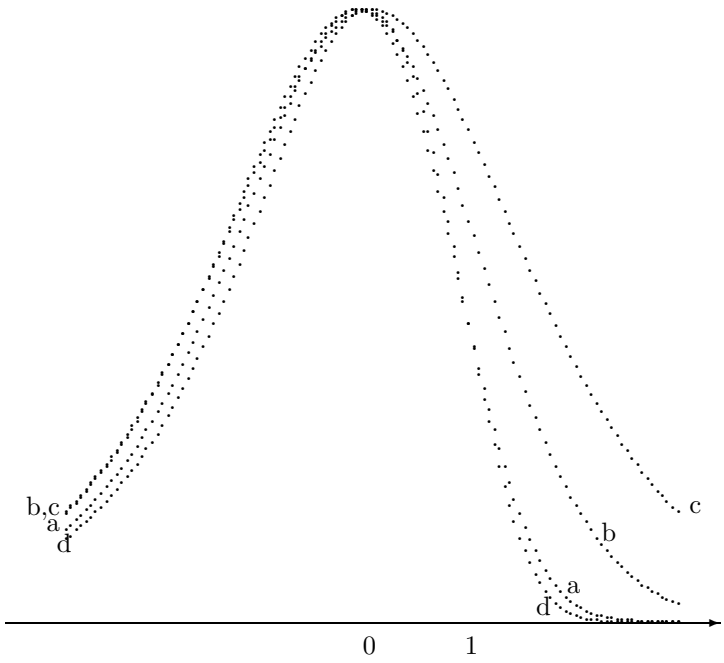

Fig. 6.8. The forms of the spectrum for the different values of the power in the integral terms of the balance equation.

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